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# Ab Initio Studies of the Interactions in Van der Waals Molecules

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## 1 Introduction

Van der Waals molecules are complexes of molecules (or atoms) which are not held together by chemical bonding, as "normal" molecules, but by weaker Van der Waals forces. One of the main reasons to study experimentally the structure and spectra of Van der Waals molecules<sup>1)</sup> is to extract (rather detailed) information about the Van der Waals interactions between the constituent molecules, information which can be used for a better understanding and description of the properties of molecular gases, liquids and solids. For small molecules, up to about ten light atoms, even more detailed information about these Van der Waals interactions<sup>1</sup> can presently be obtained from ab initio calculations, i.e. directly from the approximate solution of Schrödinger's equation by variational or perturbational methods. The accuracy of the results is still a matter of concern, since the interactions are very small relative to the molecular total or (internal) binding energies and calculational errors which are larger than the Van der Waals binding energies are easily introduced. The collaboration between theory and experiment is here very useful: the experiment can serve as a check on the accuracy of the calculations. On the other hand, theoretical results can help in the interpretation of the spectra. Thus, experiment and theory can both be improved and the combined experience for small molecules can lead to physically justified, empirically parametrized model potentials for molecules larger than those for which the ab initio calculations are feasible.

Several books and review articles<sup>2-13)</sup> are concerned with Van der Waals interactions. In the present survey, we shall first describe which are the interaction mechanisms that hold Van der Waals molecules together and we shall concentrate on the dependence of these interactions on the orientations of the constituent molecules (at longer and shorter distances, sect. 2). Then, we outline some ab initio methods enabling reasonably accurate quantitative calculations of these interactions and we discuss possible sources of errors (sect. 3), some of which can be serious. Next, in section 4, we look at some results of ab initio calculations and their bearing on the structure and dynamics of Van der Waals molecules, after first dealing with some problems occurring in the representation of the ab initio results by analytical model potentials. The final section 5 describes the effect of intermolecular interactions on some properties of Van der Waals molecules other than the energy, and the quantitative calculation of these properties. Specifically, we discuss the interaction dipole moment and the interaction induced change in the polarizability, which are of importance for the intensities in infrared absorption and (inelastic) light scattering (Raman spectra); these are connected with the inter- and intramolecular vibrations in Van der Waals molecules.

We shall compare our (ab initio) results with experimental data, but we shall not deal in this paper with empirical or semiempirical determinations of Van der Waals interactions, since these are extensively described in the other surveys<sup>1-13)</sup>.

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<sup>1</sup> In many texts, the name Van der Waals interactions is reserved for the attractive long range forces between (neutral) molecules and, often, one only includes the leading  $R^{-6}$  term in the interaction energy; we use the name in a broader sense, meaning all the attractive and repulsive interactions between chemically non-bonding molecules (cf. sect. 2).



## 2 Mechanisms of Van der Waals Interactions; Distance and Orientational Dependence

The forces between the closed shell molecules in their electronic ground states (which are the constituents of most Van der Waals molecules studied at present) are of Coulombic origin. By this we mean that they originate from the Coulomb operator, describing the interaction between the electrons and nuclei in the complex. Even for (light) open-shell molecules, such as NO or O<sub>2</sub>, the interactions between the magnetic spin and orbital momenta are expected to be smaller by several orders of magnitude than the electrostatic forces<sup>14)</sup>. Relativistic (retardation) effects can be neglected for the distances of interest in Van der Waals molecules<sup>14)</sup>. Therefore, the system of interacting molecules can be described by the time-independent non-relativistic Schrödinger equation. Practically always, when no electronic excitations or chemical reactions are considered, one can solve this Schrödinger equation in the Born-Oppenheimer approximation, i.e. one first obtains an effective potential for the nuclei by solving the equation for the electronic motion in the clamped nuclei approximation and then one calculates the nuclear (vibrational and rotational) states in this potential. Finally, in most work on intermolecular forces the rigid molecule approximation is made, i.e. it is assumed that the forces holding the nuclei together within one molecule are so much stronger than the intermolecular forces that the intramolecular and the intermolecular nuclear motions can be decoupled. Looking for example at ethylene (C<sub>2</sub>H<sub>4</sub>) molecules (sect. 4), the frequencies of the internal vibrations range from 3100 cm<sup>-1</sup> (C—H stretch) to 810 cm<sup>-1</sup> (out of plane bending), while we expect the C<sub>2</sub>H<sub>4</sub>—C<sub>2</sub>H<sub>4</sub> vibrations in a Van der Waals molecule to lie below 150 cm<sup>-1</sup>.

### 2.1 Distance and orientational dependence

Consider two rigid molecules A and B, both of arbitrary shape. Let  $\vec{R} = (R, \underline{\Omega}) = (R, \Theta, \Phi)$  be the vector pointing from the center of mass of A to the center of mass of B. The coordinates of  $\vec{R}$  are measured with respect to a space-fixed frame. Let the orientation of molecule A be described by the Euler angles  $\underline{\omega}_A = (\alpha_A, \beta_A, \gamma_A)$ , which are the angles associated with an (active) rotation of the molecule from an initial position in which a reference frame fixed on A is parallel to the space-fixed frame, to its present position. Similarly, the orientation of B is determined by the Euler angles  $\underline{\omega}_B = (\alpha_B, \beta_B, \gamma_B)$ . The interaction energy between A and B is most generally described by the following expansion<sup>15, 16)</sup>:

$$\Delta E^{AB}(\underline{\omega}_A, \underline{\omega}_B, \vec{R}) = \sum_{\Lambda} \Delta E_{\Lambda}(R) A_{\Lambda}(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) \quad (1a)$$

where  $\Lambda \equiv (L_A, K_A, L_B, K_B, L)$  is the combination of “quantum numbers” applicable to the system A—B of interest, see table 1. The angular functions are defined as:

$$\begin{aligned} A_{\Lambda}(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) &\equiv A_{L_A, K_A, L_B, K_B, L}(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) \\ &= \sum_{M_A, M_B, M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} D_{M_A, K_A}^{L_A}(\underline{\omega}_A)^* D_{M_B, K_B}^{L_B}(\underline{\omega}_B)^* C_M^L(\underline{\Omega}). \end{aligned} \quad (1b)$$



**Table 1.** Angles and quantum numbers specifying the orientational dependence of the interaction energy  $\Delta E^{AB}$ , formula (1)

A	B	angular coordinates <sup>a</sup> ( $\omega_A, \omega_B, \Omega$ )	volume of angular coordinate space <sup>a</sup> V	quantum numbers <sup>b</sup> $\Lambda$
general molecule	general molecule	$\alpha_A, \beta_A, \gamma_A, \alpha_B, \beta_B, \gamma_B, \Theta, \Phi$	$256\pi^5$	$L_A, K_A, L_B, K_B, L$
linear <sup>c</sup> molecule	general molecule	$\alpha_A, \beta_A, \alpha_B, \beta_B, \gamma_B, \Theta, \Phi$	$128\pi^4$	$L_A, L_B, K_B, L (K_A = 0)$
atom	general molecule	$\alpha_B, \beta_B, \gamma_B, \Theta, \Phi$	$32\pi^3$	$L_B, K_B (L_A = K_A = 0;$ $L = L_B)$
linear <sup>c</sup> molecule	linear <sup>c</sup> molecule	$\alpha_A, \beta_A, \alpha_B, \beta_B, \Theta, \Phi$	$64\pi^3$	$L_A, L_B, L (K_A = K_B = 0)$
atom	linear <sup>c</sup> molecule	$\alpha_B, \beta_B, \Theta, \Phi$	$16\pi^2$	$L_B (L_A = K_A = K_B = 0;$ $L = L_B)$
atom	atom	$\Theta, \Phi$	$4\pi$	$— (L_A = K_A = L_B = K_B$ $= L = 0)$

<sup>a</sup> One can choose a special coordinate system such that, for instance,  $\Theta = \Phi = \alpha_B = 0$ . So one needs a maximum of 5 (internal) angles in order to fix the (relative) orientations of the molecules in a dimer AB. This reduces the volume V by a factor of  $8\pi^2$  (or  $4\pi$  in the atom—atom case)

<sup>b</sup> From the behaviour of the angular functions (1b) under inversion of the total system, it follows that the summation (1a) over the quantum numbers  $\Lambda$  can be restricted to even values of  $(L_A + L_B + L)$ . If the molecules A or B have finite symmetry groups,  $\Lambda$  can be further restricted. For instance, if they have a center of inversion only terms with even  $L_A$  or  $L_B$  contribute. If A and B are identical molecules one can derive that:

$$\Delta E_{L_B, K_B, L_A, K_A, L} = (-1)^{L_A + L_B} \Delta E_{L_A, K_A, L_B, K_B, L}$$

Relevant information can be found also in refs.<sup>15) and 37)</sup>

<sup>c</sup> For linear molecules the remaining Euler angles can be chosen such that they coincide with the polar angles:  $\alpha_A \equiv \phi_A, \beta_A \equiv \theta_A; \alpha_B \equiv \phi_B, \beta_B \equiv \theta_B$

The functions  $\{D_{M_A, K_A}^{L_A}(\omega_A); M_A = -L_A, \dots, L_A, K_A = -L_A, \dots, L_A\}$  constitute a  $(2L_A + 1)$ -dimensional matrix  $\underline{D}^{L_A}(\omega_A)$  which represents the rotation  $\omega_A$  of molecule A. The set of these matrices forms a  $(2L_A + 1)$ -dimensional irreducible representation of the rotation group  $SO(3)$ <sup>17)</sup>. In the active rotation convention, which we are using, the rotation matrices are given by<sup>17, 18)</sup>:

$$D_{M_A, K_A}^{L_A}(\omega_A) = e^{-i\alpha_A M_A} d_{M_A, K_A}^{L_A}(\beta_A) e^{-i\gamma_A K_A} \quad (2)$$

where  $d_{M_A, K_A}^{L_A}(\beta_A)$  is a Wigner d-function<sup>17)</sup>. The rotation matrices of molecule B are defined analogously. The symbol  $\begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix}$  stands for a 3-j coefficient and



$C_M^L(\underline{\Omega})$  is a Racah spherical harmonic, in the phase of Condon and Shortley, which can also be written as a special ( $K = 0$ ) rotation matrix<sup>17)</sup>:

$$C_M^L(\underline{\Omega}) = \left( \frac{4\pi}{2L+1} \right)^{1/2} Y_M^L(\Theta, \Phi) = D_{M,0}^L(\Phi, \Theta, 0). \quad (3)$$

This property (3) and the presence of the 3-j symbol in (1b) makes the angular functions scalar, i.e. invariant under rotations of the total system (see Appendix). They span the complete space of scalar functions depending on  $\underline{\omega}_A$ ,  $\underline{\omega}_B$  and  $\underline{\Omega}$  due to the completeness of the rotation matrices in the Hilbert space  $L^2[SO(3)]$  (Peter-Weyl theorem<sup>19)</sup>). The expansion, (1), is most convenient for molecular scattering calculations as well as for the solution of the nuclear motion problem in Van der Waals molecules (in terms of coupled translational and rotational vibrations of the rigid molecules), since it leads to a maximum separation of variables in the differential equations to be solved and it allows the power of angular momentum techniques to be employed.

For linear molecules A and B, where the interaction energy does not depend on the Euler angles  $\gamma_A$  and  $\gamma_B$ , only terms with  $K_A = K_B = 0$  contribute and one can use (3) to obtain a simplified expression for (1)<sup>20)</sup> (see also table 1):

$$\Delta E^{AB}(\theta_A, \phi_A, \theta_B, \phi_B, \vec{R}) = \sum_{L_A, L_B, L} \Delta E_{L_A, L_B, L}(R) A_{L_A, L_B, L}(\theta_A, \phi_A, \theta_B, \phi_B, \Theta, \Phi) \quad (4a)$$

with angular functions:

$$A_{L_A, L_B, L}(\theta_A, \phi_A, \theta_B, \phi_B, \Theta, \Phi) = \sum_{M_A, M_B, M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \times C_{M_A}^{L_A}(\theta_A, \phi_A) C_{M_B}^{L_B}(\theta_B, \phi_B) C_M^L(\Theta, \Phi). \quad (4b)$$

If one of the molecules, say A, is an atom in an S-state only the terms with  $L_A = 0$  ( $L = L_B$ ) remain in (1) or (4). The same holds if we want to average over all orientations of one molecule, or, equivalently, put one molecule in the "unperturbed" rotational  $J = 0$  state. When averaging over the orientations of both molecules, of course, only the isotropic contribution  $\Delta E_{\text{isotropic}}^{AB} = \Delta E_{0,0,0,0,0}(R)$  remains.

In practical calculations of the intermolecular interaction potential one often chooses a special coordinate system with the z-axis parallel to  $\vec{R}$  and such that  $\alpha_B = 0$ , which simplifies the angular functions (1b) and (4b), while still retaining all the dynamical coefficients  $\Delta E_A(R)$ . This simplification is easily introduced remembering that<sup>17)</sup>:

$$C_M^L(0, 0) = \delta_{M,0} \quad (\text{Kronecker delta}), \text{ independently of } L. \quad (5)$$

## 2.2 Model potentials

The dynamical coefficients  $\Delta E_A(R)$ , which are functions of the intermolecular distance only, fully determine the orientational dependence of the interaction potential. If one wishes to derive these functions from experimental data one has to replace them by



relatively simple parametrized analytical or numerical forms. The simplest and most popular ones are:

a Lennard-Jones

$n = 6$  potential,

mostly with  $n = 12$ :  $\Delta E_{\Lambda}(R) = A_{\Lambda} R^{-n} - B_{\Lambda} R^{-6}$  (6)

a Buckingham

$\exp -6(-8)$  potential:  $\Delta E_{\Lambda}(R) = A_{\Lambda} \exp(-B_{\Lambda} R) - C_{\Lambda} R^{-6} - D_{\Lambda} R^{-8}$  (7)

but many other forms have been used, see the review by Pauly<sup>21)</sup>.

In spite of the simple form of these distance functions and the usual assumption that the angular expansion can be truncated after very few terms (for instance, only the isotropic and the first anisotropic  $L_A, L_B \neq 0$  terms), the number of parameters is mostly too large and these parameters are too strongly interdependent in affecting the measured properties, for a fully experimental determination of these parameters to be possible. Only for very simple systems such as atom-diatom systems<sup>22-27)</sup> or atom-tetrahedral molecule systems<sup>28)</sup> the experimental data could be used to yield a parametrized anisotropic potential of the form (1) and even there it appeared advantageous to extract part of the parameters<sup>29, 30)</sup> from ab initio calculations. For other molecular systems only isotropic potentials<sup>2</sup> are known<sup>21)</sup>, mostly in simplified forms such as (6) or (7).

Therefore, if one needs an anisotropic potential one often includes only specific anisotropic contributions, e.g. the molecular quadrupole-quadrupole interaction<sup>32)</sup>, making the ad hoc assumption that all other anisotropic terms are small, or one invokes model potentials with fewer parameters which are intrinsically anisotropic. Examples of the latter are:

- the atom-atom potential, which assumes additive pair-wise isotropic interactions between the atoms  $p$  and  $q$  belonging to the different molecules ( $r_{pq}$  are the atom-atom distances):

$$\Delta E^{AB} = \sum_p^{\epsilon A} \sum_q^{\epsilon B} \Delta E(r_{pq}) \quad (8)$$

with  $\Delta E(r_{pq})$  being, for instance, a Lennard-Jones potential (6) or a Buckingham potential (7) (with  $\Lambda = 0$ ).

- elliptical scalings of isotropic molecule-molecule potentials<sup>33-36)</sup>, for instance, a Buckingham  $\exp -6$  potential (7) for  $\Lambda = 0$  with the parameters  $A_0$  and  $C_0$  being simple function of the angles  $\omega_A$  and  $\omega_B$ . (9)

The specific approximations which lie at the basis of these model potentials have to be justified, however, and they are not necessarily physically realistic. Actually, the truncated angular expansion of the potential (1), with parametrized functions  $\Delta E_{\Lambda}(R)$  is a model potential also, which has to be verified.

Model potentials of the form (8) and (9) implicitly contain all the higher angular terms in (1) (with  $L_A, L_B$  up to infinity). Since the angular functions form an

<sup>2</sup> For atomic systems this is of course all one needs. Especially in the case of rare gases the (isotropic) potentials are known quite accurately<sup>31)</sup>.



orthogonal set, one can explicitly calculate the dynamic coefficients  $\Delta E_A$  for any known potential  $\Delta E^{AB}$  by integrating over all angular coordinates:

$$\Delta E_A(R) = V^{-1} (2L_A + 1) (2L_B + 1) (2L + 1) \langle A_A(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) | \Delta E^{AB}(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) \rangle \quad (10)$$

with  $A_A$  being the angular expansion functions (1b) and  $V$  the total volume of the angular coordinate space, see table 1. In general, this integration must be carried out numerically; for specific model potential  $\Delta E^{AB}$  analytical expressions have been derived<sup>36-38</sup>, using angular momentum techniques.

### 2.3 Contributions to the Interaction Energy

Although the intermolecular forces which we consider here are all of electrostatic origin (in the broad sense used in the first paragraph of this section), we can distinguish different mechanisms which contribute to the interaction energy, and to other properties of Van der Waals molecules as well (see sect. 5). Let us denote the ground state electronic wave functions of the isolated (closed shell) molecules A and B by  $|0^A\rangle$  and  $|0^B\rangle$  and the corresponding “unperturbed” electron density distributions by  $\rho_0^A$  and  $\rho_0^B$ . The excited eigenfunctions of the molecular hamiltonians  $H^A$  and  $H^B$  we denote by  $|a^A\rangle$  and  $|b^B\rangle$  with corresponding eigenvalues  $E_a^A$  and  $E_b^B$ . For the interacting system we write the perturbation operator  $V^{AB}$  as:

$$V^{AB} = H - H^A - H^B \\ = \sum_i^{\epsilon A} \sum_j^{\epsilon B} \frac{Z_i Z_j}{r_{ij}}, \quad (11)$$

the electrostatic interaction between all particles, electrons and nuclei, with charges  $Z_i$  and  $Z_j$ , belonging to A and B respectively.

#### 2.3.1 Electrostatic; Long Range Multipole Interactions, Penetration Effects

The first order, electrostatic, interaction energy is defined as:

$$\Delta E_{\text{elec}}^{(1)} = \langle 0^A 0^B | V^{AB} | 0^A 0^B \rangle = \iint \rho_0^A V^{AB} \rho_0^B d\vec{r}_A d\vec{r}_B \quad (12)$$

which corresponds with the classical Coulomb interaction energy between the unperturbed molecular charge clouds. If these charge clouds do not overlap we can make a multipole expansion of this Coulomb energy or, equivalently, of the interaction operator  $V^{AB}$ <sup>39-41</sup>:

$$V^{AB} = \sum_{l_A, l_B=0}^{\infty} (-1)^{l_A} \left[ \frac{(2l_A + 2l_B + 1)!}{(2l_A)! (2l_B)!} \right]^{1/2} R^{-l_A-l_B-1} \\ \times \sum_{m_A=-l_A}^{l_A} \sum_{m_B=-l_B}^{l_B} \sum_{m=-l_A-l_B}^{l_A+l_B} \begin{pmatrix} l_A & l_B & l_A+l_B \\ m_A & m_B & m \end{pmatrix} C_m^{l_A+l_B}(\underline{\Omega}) \tilde{Q}_{m_A}^{l_A}(\vec{r}_A) \tilde{Q}_{m_B}^{l_B}(\vec{r}_B). \quad (13)$$



The multipole operators are here defined as spherical tensors<sup>17) 3</sup>:

$$Q_{m_A}^{l_A}(\vec{r}_A) \equiv \sum_i^{\varepsilon_A} Z_i r_{iA}^{l_A} C_{m_A}^{l_A}(\theta_{iA}, \phi_{iA}), \quad (14)$$

and analogously for B, in local coordinate systems of the molecules A and B respectively, which are parallel to the global space fixed coordinate system. Multipole moments are defined (and calculated) in a molecular (body fixed) frame, however, and therefore it is convenient to convert the multipole operators to this frame also. The frames of the molecules A and B are rotated by the angles  $\omega_A$  and  $\omega_B$  with respect to the space fixed frame and we can use the following property of the spherical multipole tensors (and the unitarity of the rotation matrices)<sup>17)</sup>

$$\begin{aligned} \tilde{Q}_{m_A}^{l_A} &= \sum_{m'_A} Q_{m'_A}^{l_A} D_{m'_A, m_A}^{l_A}(\omega_A^{-1}) \\ &= \sum_{m'_A} Q_{m'_A}^{l_A} D_{m'_A, m_A}^{l_A}(\omega_A)^* \end{aligned} \quad (15)$$

where  $Q_{m'_A}^{l_A}$  are the multipole operators defined in the molecular frame of A and the  $\tilde{Q}_{m_A}^{l_A}$  are the ones appearing in the expansion (13). The moments on B transform analogously. Substituting this relation into the multipole expansion (13) and this expansion into (12), the expression for  $\Delta E_{\text{elec.}}^{(1)}$  immediately fits into the general expansion formula, (1). The dynamic coefficients in (1) obtain the closed form:

$$\begin{aligned} \Delta E_{\text{mult.}}^{(1)}{}_{L_A, K_A, L_B, K_B, L} &= (-1)^{L_A} \left[ \frac{(2L_A + 2L_B + 1)!}{(2L_A)! (2L_B)!} \right]^{1/2} \\ &\times \delta_{L_A + L_B, L} R^{-L_A - L_B - 1} \langle 0^A | Q_{K_A}^{L_A} | 0^A \rangle \langle 0^B | Q_{K_B}^{L_B} | 0^B \rangle, \end{aligned} \quad (16)$$

which represents the interaction between the  $K_A$  component of a permanent multipole moment ( $2^{L_A}$ -pole) on A and the  $K_B$  component of a permanent  $2^{L_B}$ -pole on B, varying as  $R^{-L_A - L_B - 1}$  with distance.

For real molecules A and B the charge clouds have exponential tails so that there is always some overlap and the expansion (16) is an asymptotic series<sup>43,44</sup>. Still, for the long range the multipole approximation to  $\Delta E_{\text{elec.}}^{(1)}$  can be quite accurate, if properly truncated (for instance, after the smallest term). For shorter distances, the penetration between the molecular charge clouds becomes significant, the screening of the nuclei by the electrons becomes incomplete even for neutral molecules, and the power law for  $\Delta E_{\text{elec.}}^{(1)}$  is modified by contributions which increase exponentially with decreasing R. These penetration contributions we define as:

$$\Delta E_{\text{pen.}}^{(1)} = \Delta E_{\text{elec.}}^{(1)} - \Delta E_{\text{mult.}}^{(1)}, \quad (17)$$

<sup>3</sup> For relations with Cartesian tensors, see ref.<sup>42</sup>.



with the "exact" electrostatic energy  $\Delta E_{\text{elec}}^{(1)}$  calculated according to (12) using the exact interaction operator (11), and  $\Delta E_{\text{mult.}}^{(1)}$  obtained by summing an appropriate number of multipole interaction terms (16). A simple illustration of the occurrence of these penetration interactions is given by the example of two rare gas atoms, where  $\Delta E_{\text{mult.}}^{(1)}$  is exactly equal to zero (term by term), while  $\Delta E_{\text{elec}}^{(1)}$  is not, if the charge clouds penetrate each other.

### 2.3.2 Induction, Dispersion; Multipole Interactions, Penetration Effects

The second order interaction energy, according to Rayleigh-Schrödinger perturbation theory is given by:

$$\Delta E^{(2)} = \sum_{a,b \neq 0,0} \frac{|\langle 0^A 0^B | V^{AB} | a^A b^B \rangle|^2}{E_0^A + E_0^B - E_a^A - E_b^B}. \quad (18)$$

Higher order terms can be defined as well, but what little experience is available has taught us that they are generally smaller by at least an order of magnitude. Still, they can be important if we look at specific effects such as the non-pairwise additive components to the interaction energy in Van der Waals trimers or multimers (cf. the last part of this section). In the second order summation over excited states (18) we can separate three different contributions:

$$\begin{aligned} \Delta E^{(2)} &= \sum_{a,b \neq 0,0} \dots \\ &= \sum_{\substack{a=0 \\ b \neq 0}} \dots + \sum_{\substack{a \neq 0 \\ b=0}} \dots + \sum_{\substack{a \neq 0 \\ b \neq 0}} \dots \\ &= \Delta E_{\text{ind. B}}^{(2)} + \Delta E_{\text{ind. A}}^{(2)} + \Delta E_{\text{disp.}}^{(2)}. \end{aligned} \quad (19)$$

It is easy to see that the first term corresponds with the classical polarization (or induction) energy of molecule B in the electric field of the electronic charge distribution  $q_0^A$  plus the nuclei of A, the second term with the induction energy of molecule A in the field of  $q_0^B$  plus the nuclei of B, while the third term, the dispersion energy, has no classical equivalent.

For the long range we may again substitute the multipole expansion (13) for  $V^{AB}$  and the rotation relation of the multipole operators (15), but, in contrast with the first order multipole interaction energy, the resulting expression does not immediately correspond with the general formula, (1). After recoupling the spherical tensors<sup>41)</sup>, the simple orientational dependence of (1) is recovered, however, and we find the following expressions for the dynamic coefficients<sup>45)</sup>:

$$\begin{aligned} \Delta E_{\text{ind. A, mult.}}^{(2)} &= \sum_{l_A, l'_A, l_B, l'_B} -1/2 \zeta_{l_A, l'_A, l_B, l'_B}^{L_A, L_B, L} R^{-l_A - l'_A - l_B - l'_B - 2} \\ &\quad \times \alpha_{(l_A, l'_A) L_A, K_A} [\langle 0^B | \underline{Q}^{l_B} | 0^B \rangle \otimes \langle 0^B | \underline{Q}^{l'_B} | 0^B \rangle]_{K_B}^{L_B}, \end{aligned} \quad (20)$$



an analogous expression for  $\Delta E_{\text{ind. B}}^{(2)}$  and:

$$\begin{aligned} \Delta E_{\text{disp., mult.}}^{(2)} = & \sum_{L_A, K_A, L_B, K_B, L} \sum_{l_A, l'_A, l_B, l'_B} - \zeta_{l_A, l'_A, l_B, l'_B}^{L_A, L_B, L} R^{-l_A - l'_A - l_B - l'_B - 2} \\ & \times \sum_{a \neq 0} \sum_{b \neq 0} (E_a^A - E_0^A + E_b^B - E_0^B)^{-1} \\ & \times [\langle 0^A | \underline{Q}^{l_A} | a^A \rangle \otimes \langle a^A | \underline{Q}^{l'_A} | 0^A \rangle]_{K_A}^{L_A} \\ & \times [\langle 0^B | \underline{Q}^{l_B} | b^B \rangle \otimes \langle b^B | \underline{Q}^{l'_B} | 0^B \rangle]_{K_B}^{L_B} \end{aligned} \quad (21)$$

The irreducible (spherical) multipole polarizabilities are defined as <sup>41,42</sup>:

$$\alpha_{(l_A, l'_A) L_A, K_A} = 2 \sum_{a \neq 0} (E_a^A - E_0^A)^{-1} [\langle 0^A | \underline{Q}^{l_A} | a^A \rangle \otimes \langle a^A | \underline{Q}^{l'_A} | 0^A \rangle]_{K_A}^{L_A}. \quad (22)$$

The symbol  $[\cdot \otimes \cdot]$  stands for an irreducible tensor product<sup>46</sup> between two sets of tensors  $\underline{T}^l = \{T_m^l; m = -l, \dots, l\}$  and  $\underline{T}^{l'} = \{T_{m'}^{l'}; m' = -l', \dots, l'\}$ :

$$[\underline{T}^l \otimes \underline{T}^{l'}]_M^L = \sum_{m, m'} T_m^l T_{m'}^{l'} (l, m, l', m' | L, M) \quad (23)$$

with  $(l, m, l', m' | L, M)$  being a Clebsch-Gordan coefficient. The purely algebraic coefficient  $\zeta$  occurring in (20) and (21) is lengthy but straightforward to calculate:

$$\begin{aligned} \zeta_{l_A, l'_A, l_B, l'_B}^{L_A, L_B, L} = & (-1)^{l_A + l'_A} \left[ \frac{(2l_A + 2l_B + 1)! (2l'_A + 2l'_B + 1)!}{(2l_A)! (2l'_A)! (2l_B)! (2l'_B)!} \right]^{1/2} \\ & \times (2L_A + 1)^{1/2} (2L_B + 1)^{1/2} (2L + 1)^{1/2} (l_A + l_B, 0, l'_A + l'_B, 0 | L, 0) \\ & \times \left\{ \begin{matrix} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A + l_B & l'_A + l'_B & L \end{matrix} \right\}, \end{aligned} \quad (24)$$

the expression between curly brackets being a Wigner 9-j symbol<sup>17</sup>. For linear molecules all tensor components in (20), (21) and (22) with  $K_A \neq 0$  and  $K_B \neq 0$  are zero and, moreover, the permanent moments in (20) vanish for  $m_B, m'_B \neq 0$  (in a body fixed frame with the z-axis along the molecular axis). The resulting formulas, which have been presented in ref.<sup>20</sup>, are simpler<sup>4</sup>.

<sup>4</sup> The expressions (16), (20) and (21) are easily related to the more standard form of the multipole expansion:

$$\Delta E_{\text{mult.}}^{(1, 2)} = \sum_n C_n^{(1, 2)} R^{-n}$$

which becomes, for anisotropic interactions:

$$\Delta E_{\text{mult.}}^{(1, 2)}(\underline{\omega}_A, \underline{\omega}_B, \vec{R}) = \sum_n C_n^{(1, 2)}(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}) R^{-n}$$

by collecting all terms in the series (1) with  $L_A + L_B + 1 = n$  in first order, (16), and all terms with  $l_A + l'_A + l_B + l'_B + 2 = n$  in second order, (20) and (21). In the second order one can restrict the summations to  $(l_A + l'_A + L_A)$  even and  $(l_B + l'_B + L_B)$  even.



Again, for the short range, the second order energy contributions, (18), (19), calculated with the exact operator  $V^{AB}$  (11) start to deviate from the  $R$  power series expansions, (20) and (21), and we can define the penetration effects:

$$\Delta E_{\text{ind. pen.}}^{(2)} = \Delta E_{\text{ind. disp.}}^{(2)} - \Delta E_{\text{ind. mult. disp.}}^{(2)} \quad (25)$$

which increase exponentially with decreasing  $R$ .

### 2.3.3 Exchange

Another effect, one which becomes dominant for the intermolecular forces at shorter distances, is the exchange effect, related to the required antisymmetry of the (exact) many-electron space-spin wave function under electron permutations (Pauli postulate, Fermi-Dirac statistics). In Rayleigh-Schrödinger perturbation theory, which works with product functions,  $|a^A\rangle |b^B\rangle$ , that are only antisymmetric with respect to the electron permutations within the subsystems  $A$  and  $B$ , this effect is not explicitly taken into account. Still, the total perturbation series, if it converges, will sum up to the exact wave function and the corresponding exact energy including exchange effects. Although it has been shown on simple model systems that this actually holds in practice<sup>47)</sup>, convergence to the correct permutation symmetry is reached only in very high orders of perturbation theory. Moreover, there is the problem that the “exact” wave function of the system to which the Rayleigh-Schrödinger series starting with  $|0^A\rangle |0^B\rangle$  converges, cannot obey the Pauli principle due to an incorrect symmetry in the spatial electron coordinates<sup>44,48)</sup>; so, it does not correspond to a physical state of the system (in case of more than two electrons).

Therefore, one would like to modify (symmetry adapt) the normal Rayleigh-Schrödinger perturbation theory such that the exchange effects are explicitly included in the lower order interaction energy expressions. This symmetry adaptation can be achieved by means of a projection operator, the antisymmetrizer  $A$ , that, operating on any  $N$ -electron space-spin function ( $N = N^A + N^B$ ), makes this function antisymmetric under electron permutations. Furthermore, one must adapt the wave functions to the total spin operator. Using the relation between the electron spin functions, carrying representations of the group  $SU(2)$ , and the irreducible representations of the permutation group  $S_N$ , projectors  $A_S$  can be defined<sup>49)</sup> that yield directly eigenfunctions of the total spin operator  $S^2$  or their spin-free equivalents<sup>50,51)</sup>. Moreover, if the total interacting system  $AB$  contains spatial symmetry operations under which the products  $|a^A\rangle |b^B\rangle$  are not invariant,  $A_S$  can be combined with operators that project the desired spatial symmetry as well.

It is not possible, however, to simply project the product functions  $|a^A\rangle |b^B\rangle$  with  $A_S$  and then to use these functions in Rayleigh-Schrödinger perturbation theory, for two reasons. First, the projected functions  $A_S |a^A\rangle |b^B\rangle$  are not eigenfunctions of the unperturbed hamiltonian  $H_0 = H^A + H^B$  since  $H_0$ , which corresponds to a certain assignment of electrons to each subsystem  $A$  or  $B$ , does not



commute with  $A_S$ . The total hamiltonian of the interacting system  $H = H_0 + V^{AB}$  does commute with  $A_S$ , however, leading to the relation:

$$[A_S, H_0] = [V^{AB}, A_S] \neq 0. \quad (26)$$

This relation shows how the action of the antisymmetrizer can mix different orders in perturbation theory. Secondly, the projected functions  $A_S |0^A\rangle |0^B\rangle$  do not form an orthogonal set in the antisymmetric subspace of the Hilbert space  $L^2(\mathbb{R}^{3N})$ ; if we take all excited states  $|a^A\rangle$  and  $|b^B\rangle$  in order to obtain a complete set  $|a^A\rangle |b^B\rangle$ , the projections  $A_S |a^A\rangle |b^B\rangle$  form a linearly dependent set. Expanding a given (antisymmetric) function in this overcomplete set is always possible, but the expansion coefficients are not uniquely defined. How the different symmetry adapted perturbation theories that have been formulated since the original treatment by Eisenschitz and London in 1930<sup>52)</sup>, actually deal with these two problems can be read in the following reviews:<sup>53-56)</sup>. Usually, the first order interaction energy, including exchange effects, is defined by:

$$\Delta E^{(1)} = \frac{\langle 0^A 0^B | A_S V^{AB} | 0^A 0^B \rangle}{\langle 0^A 0^B | A_S | 0^A 0^B \rangle} \quad (27)$$

which, for two hydrogen atoms, corresponds with the Heitler-London interaction energy. The second and higher order energies (and the first and higher order wave functions) have different definitions in the different formalisms, however, which is related to the non-uniqueness problems mentioned above (non-uniqueness in the orders of perturbation and in the expansion coefficients of the perturbed wave functions).<sup>5</sup> To our opinion, preference to one or the other formalism should only be given on practical grounds: which perturbation expansion converges fastest, i.e. includes as much as possible the exchange contributions in the lower orders already; which expressions are easiest to evaluate. Theoretical and numerical comparisons can be found in the literature<sup>54-58)</sup>. Actually, none of the second order exchange energies has been quantitatively calculated up to now for systems larger than two beryllium atoms<sup>59)</sup>. The first order exchange energy can be defined as follows:

$$\Delta E_{\text{exch.}}^{(1)} = \Delta E^{(1)} - \Delta E_{\text{elec.}}^{(1)} \quad (28)$$

with  $\Delta E^{(1)}$  and  $\Delta E_{\text{elec.}}^{(1)}$  given by (27) and (12), respectively.

## 2.4 Interactions from Supermolecule Calculations

Because of the formal and practical problems with symmetry adapted perturbation theory, one mostly invokes variational methods applied to the total energy of the

<sup>5</sup> Physically, one can think of rather specific second order effects caused by the exchange "forces". For instance, the Pauli exchange repulsion between two closed shell systems leads to an outward polarization of the electron clouds which lowers this exchange repulsion. This energy lowering, which may be called exchange-induction energy, has indeed been found in variational calculations. The mathematical expression for this effect is not unique, however.



interacting system AB, thus performing so-called supermolecule calculations. The methods are usually the standard (ab initio) methods used also for calculating energies and wave functions of normal molecules<sup>60)</sup>, for instance the Hartree-Fock (SCF)—LCAO method possibly extended with Configuration Interaction (CI), Multi-Configuration (MC) SCF or Many-Body Perturbation Theory (MBPT). Since these methods work with fully antisymmetrized wave functions, all exchange effects are taken into account, but due to the fact that the total hamiltonian commutes with the antisymmetrizer  $A_S$  we avoid all the theoretical problems plaguing perturbation theory. The interaction energy is obtained by subtracting the subsystem energies:

$$\Delta E^{AB} = E^{AB} - E^A - E^B \quad (29)$$

and the first order interaction energy is usually defined as:

$$\Delta \tilde{E}^{(1)} = \frac{\langle A_S 0^A 0^B | H | A_S 0^A 0^B \rangle}{\langle A_S 0^A 0^B | A_S 0^A 0^B \rangle} - E^A - E^B \quad (30)$$

with  $E^A = \langle 0^A | H^A | 0^A \rangle$ ,  $E^B = \langle 0^B | H^B | 0^B \rangle$ .

It is easily demonstrated, using the commutation relation (26) and the idempotency of the (hermitean) projector  $A_S$ , that this definition of  $\Delta \tilde{E}^{(1)}$  is identical to the perturbational definition (27) of  $\Delta E^{(1)}$  if the separate molecule wave functions  $|0^A\rangle$  and  $|0^B\rangle$  are exact eigenfunctions of  $H^A$  and  $H^B$ . For approximate molecular wave functions occurring in practical calculations,  $\Delta E^{(1)}$  and  $\Delta \tilde{E}^{(1)}$  are different, although for some approximations e.g. wave functions near the Hartree-Fock limit the deviations may be very small<sup>61)</sup>. Also higher order interaction energies can be defined in a variational supermolecule treatment by making a perturbation expansion of the secular problem<sup>62)</sup>. If the supermolecule wave function is expanded in terms of antisymmetrized products  $A_S |a^A\rangle |b^B\rangle$ , as in the multistructure Valence Bond method<sup>63)</sup>, the second (and higher) order energies become identical, for the long range, to the perturbational contributions (20), (21).

Such a correspondence cannot be found, if we use, for instance, the SCF—LCAO method with molecular orbitals delocalized over the entire supermolecule. Only indirect partitionings of the interaction energy are possible then, on the basis of different calculations with and without allowing delocalization and by component analyses of the wave function<sup>64)</sup> (e.g. looking at the admixture of excited and/or ionic states to the “starting function”  $A_S |0^A\rangle |0^B\rangle$ ). One must be cautious with such partitionings since they are basis set dependent. So, for instance, what has been called the charge transfer stabilization energy, or the charge resonance energy in case of identical subsystems A and B, is a second order overlap effect which can very well be interpreted<sup>65)</sup> as the effect of charge penetration on the induction and dispersion interactions. Moreover, if the basis sets used in supermolecule calculations are too small, one finds contributions to the interaction energy which are artifacts of the calculation. An effect which is well known by now is the basis set superposition error<sup>66)</sup>, i.e. the energy lowering of each subsystem in a limited basis due to the admixture of basis functions centered on other subsystems. This is a purely mathematical effect, which automatically occurs in any variational supermolecule calculation where one allows electron delocalization. In some cal-



culations a large part of the "charge transfer stabilization energy" should probably be ascribed to this artifact.

Another important (theoretical) point to note in supermolecule calculations is that the independent particle (SCF) model applied to the supermolecule AB includes all first order and the second order induction contributions to the interaction energy, correctly accounting for exchange, but not the second order dispersion contribution. The latter can be considered as an intermolecular electron correlation effect. In principle it can be obtained from supermolecule CI (or MCSCF, or MBPT) calculations, but in practice one must be very cautious again. Especially when using delocalized wave functions, the intermolecular correlation energy may easily get lost in the intramolecular correlation energy, which is typically hundred times larger. The basis set superposition error which occurs on the CI level<sup>67,68)</sup> as well as on the SCF level<sup>63,66)</sup> and which gives a distance dependent energy lowering, must be separated from the physical interaction contributions. Practical consequences of these problems will be discussed in the next section.

## 2.5 Additivity

The question how well the different contributions to the interaction energy in a composite system are additive can be asked on three different levels. First one may ask this question with respect to the different components (electrostatic, induction, dispersion, exchange) of the intermolecular (A—B) potential. If they were all calculated by standard (Rayleigh-Schrödinger) perturbation theory using the same interaction operator  $V^{AB}$  they would be exactly additive. Usually the "long range" contributions (electrostatic, induction, dispersion) are obtained from Rayleigh-Schrödinger perturbation theory, (mostly with the multipole expansion for  $V^{AB}$ ), but the exchange effects are neglected then. In symmetry adapted perturbation theory the latter appear as modifications of the electrostatic, induction and dispersion energies; they can be additively separated by using definitions such as (28) for the first order exchange energy. In practice, the exchange contributions are mostly obtained from supermolecule calculations, together with electrostatic and induction energies in supermolecule SCF, or together with the electrostatic energy in  $\Delta\tilde{E}^{(1)}$  (30). Then one can ask whether it is allowed to add dispersion (and induction) energies, calculated by second order perturbation theory. In other words, how large are the exchange-dispersion and exchange-induction energies? Are these not partially included in the supermolecule treatment already? And, if one uses the multipole expansion for the second order energies, how important is the additional neglect of the second order penetration energy (25)? The few data available for very small systems such as  $\text{He}_2$ <sup>54, 69, 70)</sup> and  $\text{Be}_2$ <sup>59)</sup> indicate that these second order exchange and penetration energies, in contrast with their first order counterparts (see section 3), are not very important (less than about 10% of the total second order energy) at the Van der Waals minimum.

The second additivity problem concerns the question whether the interaction potential in Van der Waals trimers or multimers (or molecular solids or liquids) is a sum of pairwise intermolecular (A—B) potentials. This question can be considered for each component of the interaction energy. The (first order) electro-



static energy is exactly pairwise additive. The dispersion energy has a three-body component which appears in third order of perturbation theory (the Axilrod-Teller triple-dipole interaction<sup>5)</sup>, but which is only a few percent of the pair energy for distances of interest. The induction energy is not at all pairwise additive; the electric fields  $\underline{E}_A$  and  $\underline{E}_B$  originating from molecules A and B can be added, but the second order polarization energy of a third molecule C contains mixed (three body) terms of the type  $-\frac{1}{2}\underline{E}_A\alpha_C\underline{E}_B$  which can be of equal size as the quadratic terms. In many Van der Waals molecules the total induction energy is small, however, compared with the dispersion energy. The (relative) error introduced in the pairwise addition of exchange energies is of the order of the intermolecular overlap integrals; calculations on  $\text{He}_3$ ,  $\text{Ne}_3$  and  $\text{Ar}_3$ <sup>71)</sup> show that it is small at the Van der Waals minimum. This intermolecular additivity problem is more extensively discussed by Margenau and Kestner<sup>5)</sup>, by Murrell<sup>8)</sup> and by Claverie<sup>72)</sup>.

The third additivity question which is sometimes asked, regards the possibility of representing an intermolecular interaction potential as a sum of (isotropic) atom-atom potentials (8) (or bond-bond potentials). Not much is known about this question, since most of the atom-atom potentials used in practice are purely empirical. We consider this question in section 4 for  $\text{C}_2\text{H}_4-\text{C}_2\text{H}_4$  and  $\text{N}_2-\text{N}_2$  interactions on the basis of our information from ab initio calculations. Especially the exchange interaction can deviate from pairwise (atom-atom) additivity, which is not surprising as the intramolecular overlap integrals are considerable (of the order of 0.5, while the intermolecular overlap integrals are typically 0.01 at the Van der Waals minimum).

### 3 Quantitative Ab Initio Calculations

In this section we discuss the most important problems occurring when one wants to make quantitative calculations of the different interaction energy components. These components have been defined in the previous section for two molecules, denoted by A and B. We shall outline some practical methods for the calculation of pair interaction energies.

#### 3.1 Methods

##### 3.1.1 Molecular Wave Functions and Properties

The first requirement in both perturbational and variational calculations of the interaction energy, is the knowledge of the "unperturbed" molecular ground state energies,  $E_0^A$  and  $E_0^B$ , and the respective wave functions,  $|0^A\rangle$  and  $|0^B\rangle$ . For many-electron systems A and B these are necessarily approximate. If the approximate wave functions  $|0^A\rangle$  and  $|0^B\rangle$  are to be used in calculating reasonably accurate first order interaction energies according to the expressions (12), (16), (27) or (30) they must be of sufficient quality to yield good multipole moments,  $\langle 0^A | Q_{m_A}^{1A} | 0^A \rangle$  and



$\langle 0^B | Q_{m_B}^{l_B} | 0^B \rangle$ ; and, especially for the short range contributions, (17) and (28), the molecular charge distributions must be accurate in the intermolecular overlap region. For most (closed shell) systems reasonable accuracy (up to 10 or 20% error) in the interaction energies can be obtained with ab initio Hartree-Fock MO-LCAO or Roothaan wave functions<sup>73)</sup> (single configuration functions, for closed shells single Slater determinants), provided one chooses good bases of atomic orbitals (AO's). These bases must be flexible especially in the outer regions of the molecules which determine the intermolecular overlap and which are weighted rather heavily in the multipole moments, particularly the higher ones. The same, or maybe an even more pronounced, sensitivity for the outer regions is exhibited also by the second order properties. Rules for selecting such bases are given in refs.<sup>69,74-76)</sup>. The calculation of the required molecular electronic and nuclear interaction integrals and the solution of the Hartree-Fock LCAO equations can be performed routinely by any of the standard molecular SCF programs<sup>60)</sup>, usually based on Gaussian type AO's. The calculation of molecular wave functions and properties beyond the Hartree-Fock level (CI, MCSCF<sup>60)</sup>, MBPT<sup>77)</sup>) is not a routine job yet, and the application of such wave functions to the evaluation of intermolecular interaction energies is even more difficult. The calculation of the molecular multipole moments can be carried out with the properties packages that go with some of the molecular wave function programs, up to octupole ( $l = 3$ ) or hexadecapole ( $l = 4$ ) moments, or with special programs for higher  $l$  values<sup>78)</sup>. The lower multipole moments are sometimes available from experiment also.

### 3.1.2 Isotropic Long Range Interactions (Second Order)

In first order the isotropic long range interactions vanish, except when the molecules have charges (monopoles,  $l = 0$ ). The next problem in a perturbation calculation of the interaction energy without intermolecular exchange is that in the second order energy, (18) or (21), and in the polarizability, (22), occurring in (20), one has to perform an infinite summation over the complete set of excited states  $|a^A\rangle |b^B\rangle$ . The majority of the work<sup>6)</sup> on the estimation of this second order sum over excited states has been done in the multipole expansions, (20), (21), (22), where the matrix elements occurring in the numerator of  $\Delta E^{(2)}$ , (18), separate into products of monomer transition moments:  $\langle 0^A | Q_{m_A}^{l_A} | a^A \rangle$  and  $\langle 0^B | Q_{m_B}^{l_B} | b^B \rangle$ . We summarize and illustrate the available ab initio methods for calculating the isotropic dispersion energy coefficients (and polarizabilities). These coefficients can be obtained from (21) by substituting  $L_A = K_A = L_B = K_B = L = 0$  (cf. sect. 2):

$$\Delta E_{\text{disp., mult. isotropic}}^{(2)} = - \sum_{l_A, l_B} C_{2l_A + 2l_B + 2}^{\text{isotropic}} R^{-2l_A - 2l_B - 2} \quad (31a)$$

and the multipole expansion coefficients are given by:

$$C_{2l_A + 2l_B + 2}^{\text{isotropic}} = \frac{1}{4} \frac{(2l_A + 2l_B)!}{(2l_A)!(2l_B)!} \sum_{a \neq 0} \sum_{b \neq 0} (E_a^A - E_0^A + E_b^B - E_0^B)^{-1} \times (E_a^A - E_0^A)^{-1} (E_b^B - E_0^B)^{-1} f_{l_A}^{0AaA} f_{l_B}^{0BbB} \quad (31b)$$



Note that the mixed-pole terms ( $l'_A \neq l_A$  or  $l'_B \neq l_B$ ) have disappeared. The  $f_l^{0n}$  are the rotationally averaged  $2^l$ -pole oscillator strenghts:

$$f_l^{0n} = 2(2l+1)^{-1} \sum_{m=-l}^l (E_n - E_0) |\langle 0 | Q_m^l | n \rangle|^2. \quad (32)$$

Let us introduce the moments of the oscillator strength distribution<sup>79-81)</sup>. These are defined as:

$$S_l(k) = \sum_{n \neq 0} (E_n - E_0)^k f_l^{0n}. \quad (33)$$

The isotropic ( $L_A = K_A = 0$ )  $2^{l_A}$ -pole polarizability of molecule A (cf. (22)) can be written as such a moment:

$$\alpha_{l_A}^{\text{isotropic}} = S_{l_A}(-2). \quad (34)$$

The simplest (Unsöld) approximation<sup>82)</sup> to the summations occurring in the expressions, (31), (33) and (34), is made by assuming that the excitation energies ( $E_a^A - E_0^A$ ) and ( $E_b^B - E_0^B$ ) can be replaced by constant average excitation energies  $\Delta^A$  and  $\Delta^B$ . In this manner, one obtains for the (Unsöld) polarizability (34):

$$\alpha_{l_A}^{\text{isotropic}} = S_{l_A}^U(-2) = (\Delta^A)^{-1} S_{l_A}(-1) \quad (35)$$

and one can avoid the summation over excited states  $|n\rangle$  by using the closure relation (sum rule):

$$S_l(-1) = 2(2l+1)^{-1} \sum_m [\langle 0 | Q_m^{l+1} Q_m^l | 0 \rangle - |\langle 0 | Q_m^l | 0 \rangle|^2]. \quad (36)$$

The multipole coefficients in the dispersion energy (31) can now be written as:

$$C_{2l_A+2l_B}^{\text{isotropic}} = \frac{1}{4} \frac{(2l_A+2l_B)!}{(2l_A)!(2l_B)!} \frac{\Delta^A \Delta^B}{\Delta^A + \Delta^B} \alpha_{l_A}^{\text{isotr}} \alpha_{l_B}^{\text{isotr}} \quad (37)$$

which, for  $l_A = l_B = 1$ , is just London's well-known approximate expression for  $C_6$ <sup>83)</sup>. Often, one assumes that the average excitation energies  $\Delta$  can be replaced by empirical quantities, for instance the first molecular ionization energies. It is this latter assumption which has given the Unsöld approximation a rather bad reputation, since the results can be wrong by a factor of 2 (except for two hydrogen atoms where the error is less than 10%).

It is also possible to make ab initio calculations of the  $\Delta$ 's, however, and at the same time to improve the Unsöld scheme by assuming that the  $\Delta$ 's are dependent on the indices  $l$ , labelling the multipole operators ( $2^l$ -poles) associated with the excitations. Such a non-empirical Unsöld scheme has been proposed by Mulder et al.<sup>75,84,85)</sup>. The average excitation energy is defined as the ratio:

$$\Delta_l = S_l(-1)/S_l(-2) \quad (38)$$

and the moments  $S_l(k)$  are calculated for each molecule by considering all  $2^l$ -pole excitations in a finite basis set. The  $\Delta_l$ 's are then substituted into (35) and (37) and the moments  $S_l(-1)$  are computed from the sum rule expression (36), which holds



exactly for exact wave functions. An advantage of this approach is that the ratio (38) appears to be rather insensitive to the quality of the basis set; the use of the sum rule (36) effectively corrects for the incompleteness of the basis.

Similar to this non-empirical Unsöld method is the generalized Kirkwood method<sup>86-89)</sup> in its one-parameter version. Here  $\Delta_1$  is defined as:

$$\Delta_1 = S_1(0)/S_1(-1) \quad (39)$$

but the use of spectral representations (sums over excited states) is completely avoided by replacing both moments  $S_1(0)$  and  $S_1(-1)$  by their sum rule expressions, (36) for  $S_1(-1)$ . For example, in the dipole case we have the Thomas-Reiche-Kuhn sumrule<sup>80)</sup> for  $S_1(0)$ :

$$S_1(0) = N \quad (\text{number of electrons in the molecule}) \quad (40)$$

Using the Hylleraas variation principle<sup>80,90)</sup> with the (Kirkwood<sup>91)</sup>) single parameter trial function  $\lambda Q_m^1 |0\rangle$  or with multi-parameter functions, it has been proved<sup>86,89)</sup> that this method yields rigorous lower bounds to the dispersion multipole coefficients (31b) calculated from the (frequency dependent) polarizabilities via the Casimir-Polder formula<sup>6,92)</sup>. This work, especially its recent extensions to larger sets of moments  $S_l(k)$  yielding both upper and lower bounds to the dispersion coefficients<sup>88)</sup>, can be considered as an extension of the (semiempirical) methods by Langhoff, Gordon and Karplus<sup>93)</sup>, Pack et al.<sup>94)</sup> and Meath et al.<sup>95)</sup>. These authors have estimated dispersion energy coefficients from experimental oscillator strength distributions<sup>95)</sup> and optical refractivity data<sup>93,94)</sup>. This has yielded quite accurate results, but the experimental data required are only available for the dipole transitions, and so the application to higher moments must be based on ab initio calculations (cf. ref.<sup>96)</sup> for rare gas dispersion interaction coefficients).

The most direct way to approximate the infinite summations occurring in (31), (33) and (34), is to replace them by finite summations over "effective excited states"<sup>69,97,98)</sup>. In other words, the exact oscillator strength distributions of the molecules consisting of some delta functions for the discrete levels and a continuum for the ionized states, is replaced by a finite set of delta functions.<sup>6</sup> The completeness of these "effective excited states" can be tested by checking the sum rules for the moments  $S_l(k)$  (33) and the Hylleraas variation principle can be invoked again to optimize the effective excited state wave functions (using a trial function which is a finite linear combination of such functions). Just as is the case for the ground state wave functions  $|0\rangle$  one can in principle represent these excited states  $|n\rangle$  at different levels of approximation, starting from Hartree-Fock LCAO (single configuration) wave functions and then correcting for the electron repulsion (correlation). The use of well-correlated wave functions (large CI expansions) becomes extremely difficult for molecules, however, if one has to describe all the excited states  $|n\rangle$ . Even at the Hartree-Fock LCAO level the calculations are already time-consuming, since one has to use large AO bases including atomic polarization functions in

<sup>6</sup> The pseudo-state method of Margoliash et al.<sup>99)</sup> and the very simple Dalgarno refractivity scheme<sup>100)</sup> for calculating molecular  $C_6$  dispersion coefficients can be considered as empirical versions of this approach.



order to make the excited states  $|n\rangle$  satisfy the sum rules to a reasonable accuracy<sup>20, 74, 75</sup>). The calculation of the molecular transition moments  $\langle 0 | Q_m^l | n \rangle$  is relatively easy<sup>78</sup>).

### 3.1.3 Anisotropic Long Range Interactions

Some of the *ab initio* methods described in the previous section have been extended to the anisotropic interactions between molecules. For instance, the non-empirical Unsöld method, has been used<sup>75, 84, 85</sup>) with (*ab initio* calculated) average excitation energies  $\Delta_{l,m}$  that depend not only on the order  $l$  of the multipole operator associated with the excitations, but also on its components  $m$ . The method which explicitly calculates the “effective” excited state functions  $|a^A\rangle$  and  $|b^B\rangle$  has been applied<sup>20, 75, 101</sup>) to the anisotropic long range interactions, expressions (20) and (21). An advantage of the latter method is that the functions  $|a^A\rangle |b^B\rangle$  can be used also in the “exact” formula for  $\Delta E^{(2)}$ , (18), where the multipole expansion is avoided, and, thus, charge penetration effects are included in  $\Delta E^{(2)}$ .<sup>7</sup> Even one can take (higher order) exchange effects into account in a variational treatment on the basis of the antisymmetrized states  $A |a^A\rangle |b^B\rangle$ <sup>63</sup>).

Knowing the molecular permanent multipole moments and transition moments (or “closure moments” derived from sum rules, such as (36)), the computation of the first and second order interaction energies in the multipole expansion becomes very easy. One just substitutes all these multipole properties into the expressions (16), (20), (21) and (22), together with the algebraic coefficients (24) (tabulated up to  $R^{-10}$  terms inclusive in ref.<sup>20</sup>), in a somewhat different form<sup>8</sup>), and one calculates the angular functions (1b) for given orientations of the molecules.

### 3.1.4 Intermediate Range Interactions

If one wants to calculate not only the long range part of the interaction potential, but also the region including the Van der Waals minimum, one must account for short range charge penetration and exchange effects. Charge penetration is included by evaluating the expressions (12) and (18) with the exact interaction operator  $V^{AB}$ , which requires the computation of very large numbers of electronic and nuclear interaction integrals. Although this computation can be performed with any of the standard integral programs for molecular calculations<sup>60</sup>), it is a (computer) time-consuming job, especially as it has to be repeated for each dimer geometry. (In contrast with the multipole calculations where we have to repeat only the computation of the angular functions for each orientation of the molecules in the dimer.) Some time can be saved by modifying the standard programs so as to

<sup>7</sup> This could equally be done by making a spherical wave expansion for  $V^{AB}$ , as proposed by Koide<sup>102</sup>), but his method for calculating  $\Delta E^{(2)}$  is practical only for atoms.

<sup>8</sup> Although ref.<sup>20</sup>) is concerned with linear molecules, this table is also complete for the general case of arbitrary molecules.



restrict the calculation to only those interaction integrals occurring in (12) and (18). Even this advantage is lost if one wishes to include exchange effects in the first, (27) or (30), or higher order interaction energies. The number of integrals becomes the same as in a full (supermolecule) calculation of the interacting system, AB. Moreover, one has to solve the supermolecule SCF, or CI, or MCSCF, or MBPT, or CEPA problem<sup>60)</sup> or to calculate the different interaction contributions in (exchange) symmetry adapted perturbation theory<sup>53-56)</sup>. To date, such calculations are possible only for very small molecules, that is, if one does not want to make severe restrictions on the size of the basis sets or to invoke approximate calculation schemes (e.g. the Extended Hückel<sup>103)</sup>, CNDO<sup>104)</sup> or Gordon-Kim<sup>105)</sup> method), which mostly lead to such a dramatic loss of accuracy that the calculated interaction potential loses all physical significance. Some typical computer timings for different steps in the calculation of the  $N_2-N_2$  interaction potential are given in table 2. Before showing some illustrative results we discuss a few more points of practical importance.

**Table 2.** Typical computing times (CPU minutes) on IBM 370/158 (IBM 370/158  $\simeq$  CDC 6400  $\simeq$  Univac 1110) for the  $N_2-N_2$  interaction potential surface<sup>101, 136)</sup>

	Interaction energy, <sup>a</sup> including penetration and exchange		Long range interaction energy <sup>a</sup> (multipole expansion up to $R^{-10}$ terms inclusive)
Integrals	100-200	Multipole (transition) moments	3
$\Delta E^{(1)}$ (eqn. 30)	10	$\Delta E_{\text{mult.}, A}^{(1)}$ (eqn. 16)	0.01
$\Delta E^{(2)}$ (eqn. 18), no exchange	15 (55) <sup>b</sup>	$\Delta E_{\text{mult.}, A}^{(2)}$ (eqns. 20, 21)	15 (30) <sup>b, c</sup>
	125-225 min. Has to be repeated for each point on the potential surface		18 min. Potential surface can be generated by calculating $A_A(\omega_A, \omega_B, \Omega)$ , (eqn. 1 b)

<sup>a</sup> Monomer AO basis set of 72 primitive/50 contracted GTO's (9s, 5p, 2d/4s, 3p, 2d); integral time depends on distance R

<sup>b</sup> Monomer basis of 70 contracted GTO's ((basis a) + 1f)

<sup>c</sup> Reduced to 0.02 min. in the Unsöld approximation

In any (variational) supermolecule calculation which allows unconstrained mixing of basis functions centred on different molecules we obtain the so-called basis set superposition error (BSSE), the energy lowering of each subsystem by the addition of basis functions localized on other subsystems, (cf. sect. 2). This energy lowering is dependent on the dimer geometry and strongly resembles the shape of the physical interaction potential<sup>63, 67)</sup>; it is purely a numerical artifact, however, due to the fact that the monomer bases are not complete yet. The error occurs in principle at the SCF level<sup>63, 66)</sup> and, again, at the CI level<sup>67, 68, 106)</sup>. One can reduce this error by using sufficiently large and well balanced orbital bases at the SCF level and configuration bases at the CI level, so as to reach the Hartree-Fock



limit and the exact non-relativistic limit in the energies of the subsystems. At the SCF level this has now been done for dimers of small molecules ( $H_2$ ), or atoms (He, Ne), up to the point where the BSSE is small compared with the interaction energy. At the CI level even with very large CI expansions for very small systems, such as He— $H_2$ <sup>107)</sup>, the estimated error in the (ground state) correlation energy is still of the same magnitude as the Van der Waals well depth. At the SCF level one has proposed an approximate method<sup>108)</sup> to correct for the BSSE. The energies of both monomers A,  $E^{A(B)}$ , and B,  $E^{B(A)}$ , are calculated in the AO basis of the total dimer AB. These energies are then subtracted from the dimer (SCF) energy  $E^{AB}$  in order to obtain the corrected supermolecule interaction energy (cf. expression (29)):

$$\Delta E^{AB} = E^{AB} - E^{A(B)} - E^{B(A)} \quad (41)$$

This procedure has been theoretically justified<sup>109)</sup> and it appears to work numerically reasonably well<sup>109,110)</sup> if the basis sets are not too badly chosen. At the CI level similar, though somewhat more complicated, procedures have been proposed<sup>68, 106, 111)</sup>, but there is less experience available yet as to their numerical performance.

A practical way to avoid contamination of the intermolecular correlation energy (which corresponds with the dispersion interaction) with geometry dependent intramolecular contributions which are numerical artifacts (for an analysis, see ref.<sup>112)</sup>), is to express the CI wave functions in terms of orbitals localized on the monomers. By selecting the configurations one can then calculate the intermolecular correlation energy separately (in a CI or MCSCF or MBPT or CEPA calculation). For example, the multistructure VB method<sup>63)</sup> is such a CI expansion with configurations  $A|a^A\rangle|b^B\rangle$  that are built from singly excited Hartree-Fock functions  $|a^A\rangle$  and  $|b^B\rangle$  and so they only contribute to the intermolecular correlation energy (according to Brillouin's theorem<sup>113)</sup>). Actually, one should use correlated monomer wave functions,  $|a^A\rangle$  and  $|b^B\rangle$ , or, in other words, include the coupling terms between intra- and intermolecular correlations. This has been done for very small systems: He—He<sup>114,54)</sup>, He— $H_2$ <sup>115)</sup>,  $H_2$ — $H_2$ <sup>116)</sup>; it reduces the depth of the calculated Van der Waals well by about 10% in these systems. In other systems (Be, Mg, Ca atoms) where the monomer correlation energy is relatively large because of a quasi degenerate ground state and hence a single configuration wave function is a bad description, it has been found<sup>117)</sup> that the effect of using correlated wave functions on the long range dispersion coefficients,  $C_6$ ,  $C_8$ ,  $C_{10}$ , can be considerable. It is important then<sup>117)</sup> to "correlate" both the ground state  $|0\rangle$  and the excited states  $|n\rangle$  and the calculation of the full interaction potential becomes extremely difficult for all but the smallest systems.

### 3.2 Illustrative Results

We now show some representative results which illustrate the applicability of different methods for computing the intermolecular potential. We start with the long range part by looking at the first and second order multipole series (16), (20) and (21). The lowest term(s) in the first order series can be easily checked by



comparing the (ab initio) calculated multipole moments (listed for many molecules in refs.<sup>118,119</sup>) with experimental ones that are available (usually only the dipole moment, sometimes the quadrupole and very rarely, such as for  $N_2$ <sup>101</sup>), estimates for the next higher moment). For the leading second order dispersion term  $C_6 R^{-6}$  (and for the dipole polarizability  $\alpha_1$  occurring in the leading induction term) reliable semi-empirical values are available (only the isotropic ones, mostly from refractivity data<sup>93,94,100</sup> and from optical spectra, yielding dipole oscillator strength distributions<sup>95</sup>). These can be used as a standard for the ab initio methods, while the latter have the great advantage that the higher coefficients and the anisotropy can be computed as well. The higher dispersion coefficients mostly quoted in the literature, so far, have been obtained from a single harmonic oscillator model<sup>5,120,121</sup>). This model has been reported<sup>96,122,123</sup> to underestimate  $C_8$  and  $C_{10}$ , however, the more so for molecules of increasing size<sup>124,125</sup>). A more sophisticated

**Table 3.** Isotropic dispersion energy coefficients  $C_6$  and ratios  $C_8/C_6$  and  $C_{10}/C_6$  (in atomic units) for various methods, described in the text

		Ab initio		Empirical <sup>c</sup>	Single- $\Delta$ Unsöld <sup>d</sup>	Oscillator model	
		Unsöld <sup>a</sup>	Kirkwood <sup>b</sup>			Fontana <sup>e</sup>	Amos and Yoffe <sup>f</sup>
$C_6$	NH <sub>3</sub>	83.5	90.2	89.08		74	90.9
	CH <sub>4</sub>	135	158	129.6		118	142 (133)
	N <sub>2</sub> O	394	294	184.9		—	—
	C <sub>2</sub> H <sub>4</sub>	341	334	—		—	321 (357)
	C <sub>3</sub> H <sub>6</sub>	713	789	630.8		—	738
	C <sub>6</sub> H <sub>6</sub>	2670	2617	—		—	2300
$C_8/C_6$	NH <sub>3</sub>	23.3	25.2		25.6 (19.0)	11.9	12.4
	CH <sub>4</sub>	31.5	33.0		35.4 (23.3)	9.8	14.4 (14.1)
	N <sub>2</sub> O	33.3	37.1		41.2 (25.3)	—	—
	C <sub>2</sub> H <sub>4</sub>	46.7	—		—	—	14.5 (17.5)
	C <sub>3</sub> H <sub>6</sub>	60.7	64.2		64.6 (33.0)	—	14.5
	C <sub>6</sub> H <sub>6</sub>	93.6	—		—	—	18.1
$C_{10}/C_6$	NH <sub>3</sub>	672	692		726 (427)	174	188
	CH <sub>4</sub>	1109	1123		1282 (626)	118	252 (241)
	N <sub>2</sub> O	1369	1546		1776 (696)	—	—
	C <sub>2</sub> H <sub>4</sub>	2265	—		—	—	260 (398)
	C <sub>3</sub> H <sub>6</sub>	3589	3842		3905 (1211)	—	260
	C <sub>6</sub> H <sub>6</sub>	8345	—		—	—	428

<sup>a</sup> Results from refs.<sup>84</sup>) for C<sub>2</sub>H<sub>4</sub>,<sup>85</sup>) for C<sub>6</sub>H<sub>6</sub> and<sup>128 a)</sup> for NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>

<sup>b</sup> Results from refs.<sup>128 a)</sup> for NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>,<sup>128 b)</sup> for C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> calculated according to the method of ref.<sup>86</sup>)

<sup>c</sup> Accurate results from empirical dipole oscillator strength distributions for NH<sub>3</sub>, N<sub>2</sub>O and CH<sub>4</sub><sup>95</sup>); results for C<sub>3</sub>H<sub>6</sub> according to the Dalgarno refractivity scheme<sup>100</sup>) from ref.<sup>128 c)</sup>

<sup>d</sup> Results from ref.<sup>128 a)</sup> calculated with  $\Delta_1 = \Delta_2 = \Delta_3$  (equal average energies for dipole, quadrupole, octupole excitations); values in parentheses if the original single- $\Delta$  Unsöld method is used as in ref.<sup>123</sup>) with the sum rule (36) replaced by (42)

<sup>e</sup> Results from ref.<sup>121</sup>)

<sup>f</sup> Results from ref.<sup>126</sup>) for NH<sub>3</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>; results in parentheses and those for C<sub>3</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> from ref.<sup>129</sup>). In both references the actual bond oscillator model values for  $C_8$  and  $C_{10}$  were scaled upward by factors of 2 and 4, respectively; these scaled results are presented in the table



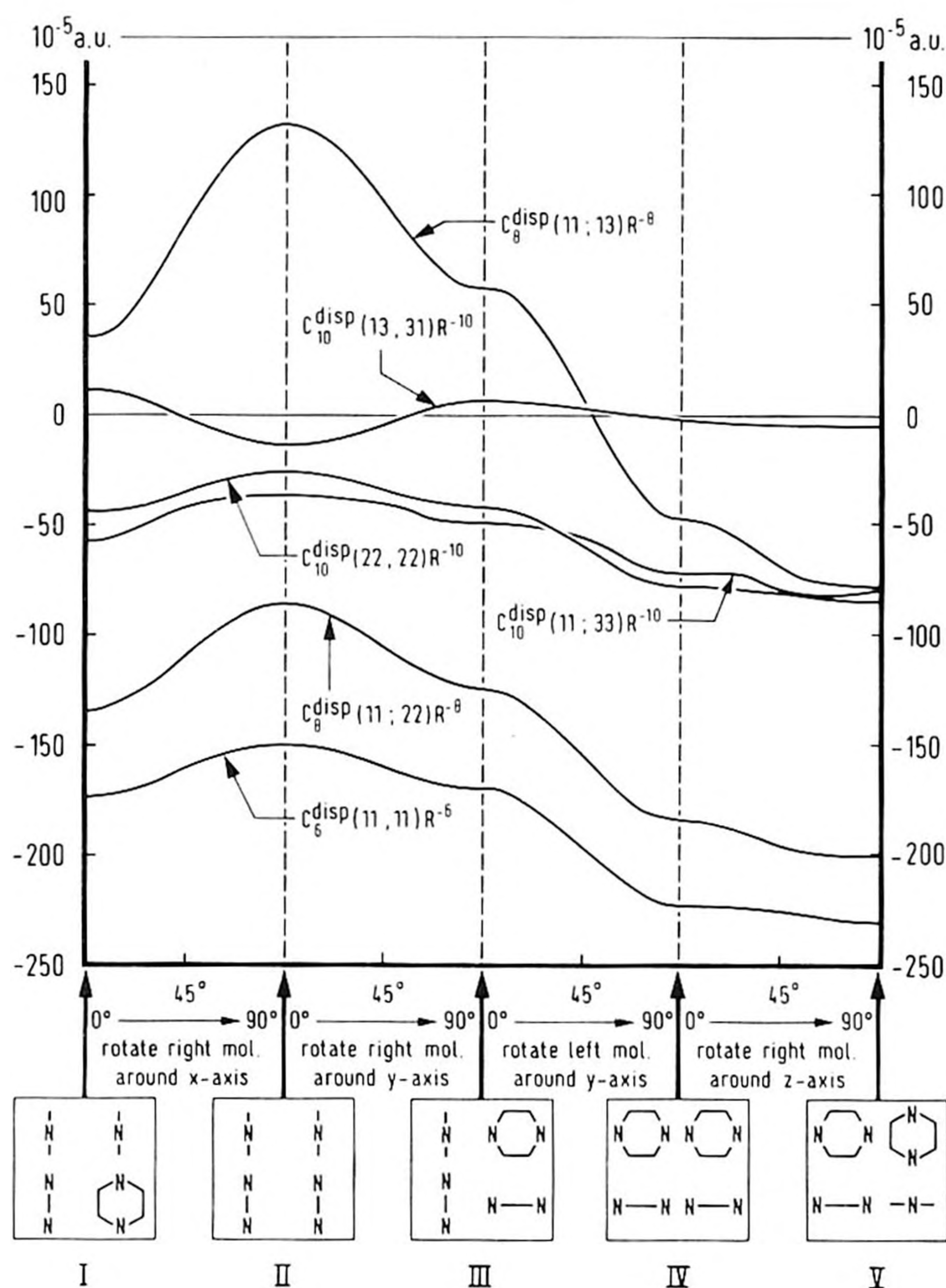
oscillator model has been introduced by Amos and Yoffe<sup>126)</sup>, who assigned different oscillators to different bonds in the molecule. A method to estimate ratios  $C_8/C_6$  and  $C_{10}/C_6$  first used by Margenau for H—H and He—He<sup>127)</sup> has been revived by Starkschall and Gordon<sup>123)</sup> in an application to rare gas atoms. This method is essentially identical with the Unsöld method mentioned above, but it assumes equal average excitation energies for the dipole, quadrupole and octupole transitions ( $\Delta_1 = \Delta_2 = \Delta_3$ ). Recently, numerical values have been computed with this “single- $\Delta$  Unsöld” method for a number of molecular systems: CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF, (for ref. see<sup>128)</sup>). In table 3 we compare the results obtained from these simplified models with results from the ab initio Unsöld and Kirkwood methods described above and with the accurate empirical data (for  $C_6$  only). For  $C_6$  the agreement is reasonable, except for N<sub>2</sub>O (for more details, see ref.<sup>128)</sup>). The ratios  $C_8/C_6$  and  $C_{10}/C_6$  are much smaller, however, in the oscillator model and in the single- $\Delta$  Unsöld method than in the ab initio Unsöld and Kirkwood schemes. These discrepancies are explained in ref.<sup>128)</sup> as being largely due to further approximations made in the bond oscillator and single- $\Delta$  Unsöld models. In the original single- $\Delta$  Unsöld scheme<sup>123)</sup> the sum rule expression (36) is replaced by

$$S_l(-1) = 2(2l + 1)^{-1} \langle 0 | \sum_i r_i^{2l} | 0 \rangle, \quad (42)$$

thus neglecting significant terms. If these terms are included<sup>128)</sup> the single- $\Delta$  Unsöld method yields ratios  $C_8/C_6$  and  $C_{10}/C_6$  which are slightly larger than the ab initio Unsöld values. In the bond oscillator model terms in  $C_8$  and  $C_{10}$  are ignored which originate from the translation of the multipole operators from the molecular center of mass to the local bond origins. This causes the unexpected result, observed in refs.<sup>126, 129)</sup>, that the ratios  $C_8/C_6$  and  $C_{10}/C_6$  hardly depend on the size of the molecules. When these translation terms are included the bond oscillator model gives somewhat more realistic  $C_8$  and  $C_{10}$  values, the remaining discrepancies being due to the shortcomings of the harmonic oscillator model itself. The ratios  $C_8/C_6$  and  $C_{10}/C_6$  obtained with the ab initio Unsöld and Kirkwood methods are probably rather accurate; they might be more reliable even than the absolute  $C_6$  values<sup>128)</sup>. The insensitivity of the Unsöld method to the size of the basis (in contrast with the methods that explicitly include the excited states) is clearly displayed in fig. 9 of ref.<sup>75)</sup>. Results calculated for H<sub>2</sub><sup>20)</sup>, N<sub>2</sub><sup>101)</sup>, C<sub>2</sub>H<sub>4</sub><sup>75, 84)</sup>, (aza)benzene(s)<sup>84, 85)</sup> by this method are quite satisfactory even for rather small bases. This figure and fig. 1 in this review also show the importance of the mixed-pole ( $l_A \neq l'_A$  or  $l_B \neq l'_B$ ) terms in the dispersion coefficients (21) higher than  $C_6$ ; they cause the higher dispersion terms to be much more anisotropic than the first term<sup>20, 101)</sup>.

After looking at the individual terms, we illustrate (on the example of two parallel ethene molecules) the convergence of the multipole series as a whole, in figs. 2 and 3, for the first order (electrostatic) and second order (dispersion) energies (16) and (21), and we compare the truncated multipole expansions with the unexpanded results, (12) and (18). The Van der Waals minimum in the isotropic potential lies at about  $R = 4.5 \text{ \AA}$  ( $8.5a_0$ ). For large distance,  $R = 6.35 \text{ \AA}$  ( $12a_0$ ), the multipole expansion accurately converges to the exact result, although the first

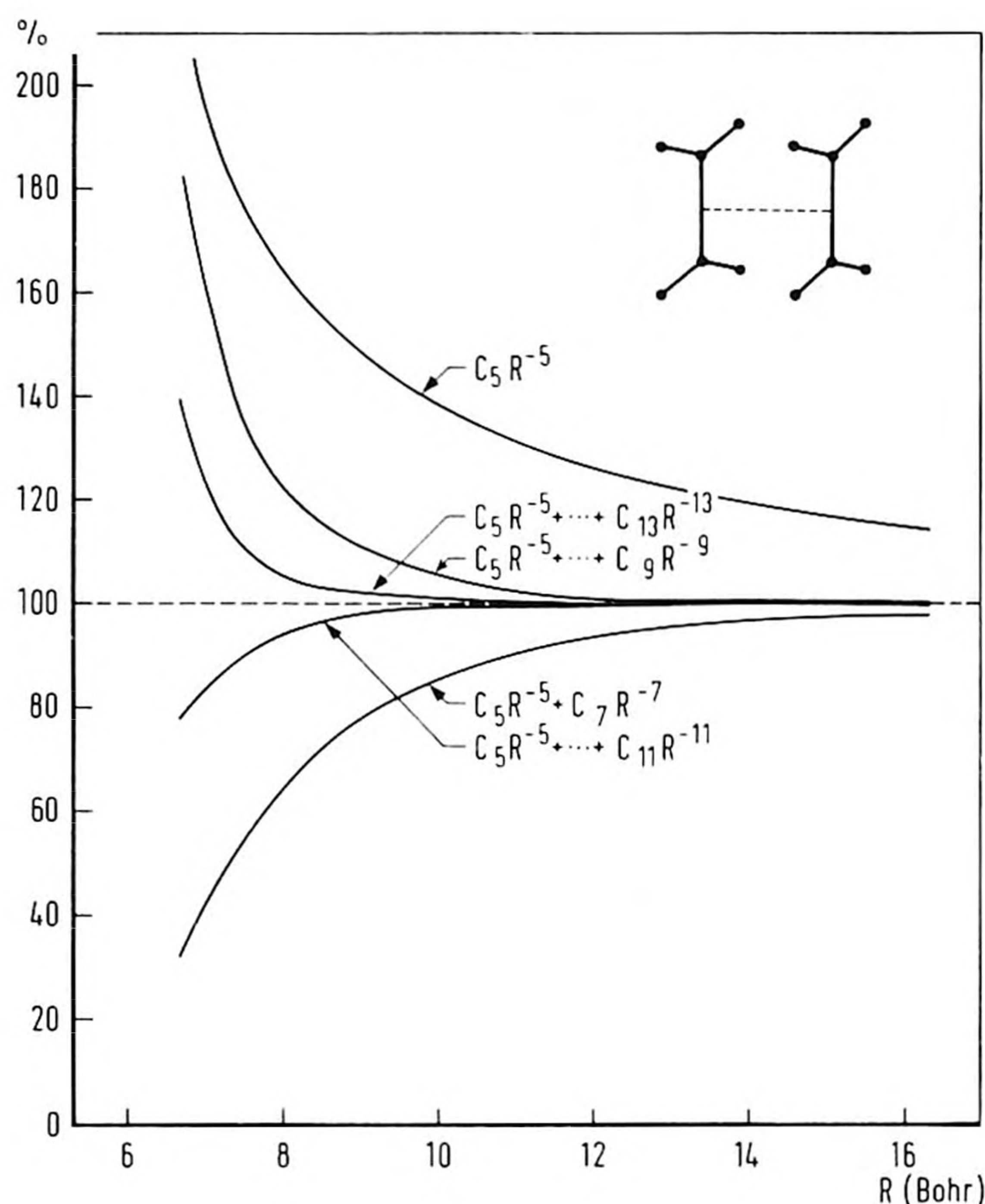




**Fig. 1.** Orientational dependence of the dispersion (multipole) interaction energy between two pyrazine molecules at  $R = 10a_0$  (from ref.<sup>84</sup>). Different 2<sup>l</sup>-pole contributions to eqn. (21) are labelled by  $(l_A l'_A; l_B l'_B)$ ; quadratic terms:  $l_A = l'_A, l_B = l'_B$ ; mixed pole terms:  $l_A \neq l'_A$  or  $l_B \neq l'_B$

term alone is in error by 25 and 10%, for the electrostatic and dispersion energies, respectively. At  $R = 4.75 \text{ \AA}$  ( $9a_0$ ) the higher terms in the multipole series are even more important (the errors in the first term are 49 and 12%), but the series seems still convergent up to the point where we have truncated. At  $R = 3.2 \text{ \AA}$  ( $6a_0$ ) the results clearly exhibit divergence of the series. Although the usual procedure of truncating the series after the smallest term and, possibly, a partial inclusion of this term<sup>130-132</sup>) might give a crude estimate of the size of the interactions, it does not look very meaningful when the divergence starts already that early in the series. An alternative procedure of using damping functions<sup>133</sup>) in order to correct the multipole series for charge penetration effects might work better, but one should realize that such damping functions probably have to be term and system dependent<sup>134, 135</sup>); then, they could only be obtained by actually evaluating the penetration effects and their use is not very helpful. We must warn for cases (a trivial one is the rare gas atom-atom interaction) where the multipole expansion does seem to converge, while the sum still





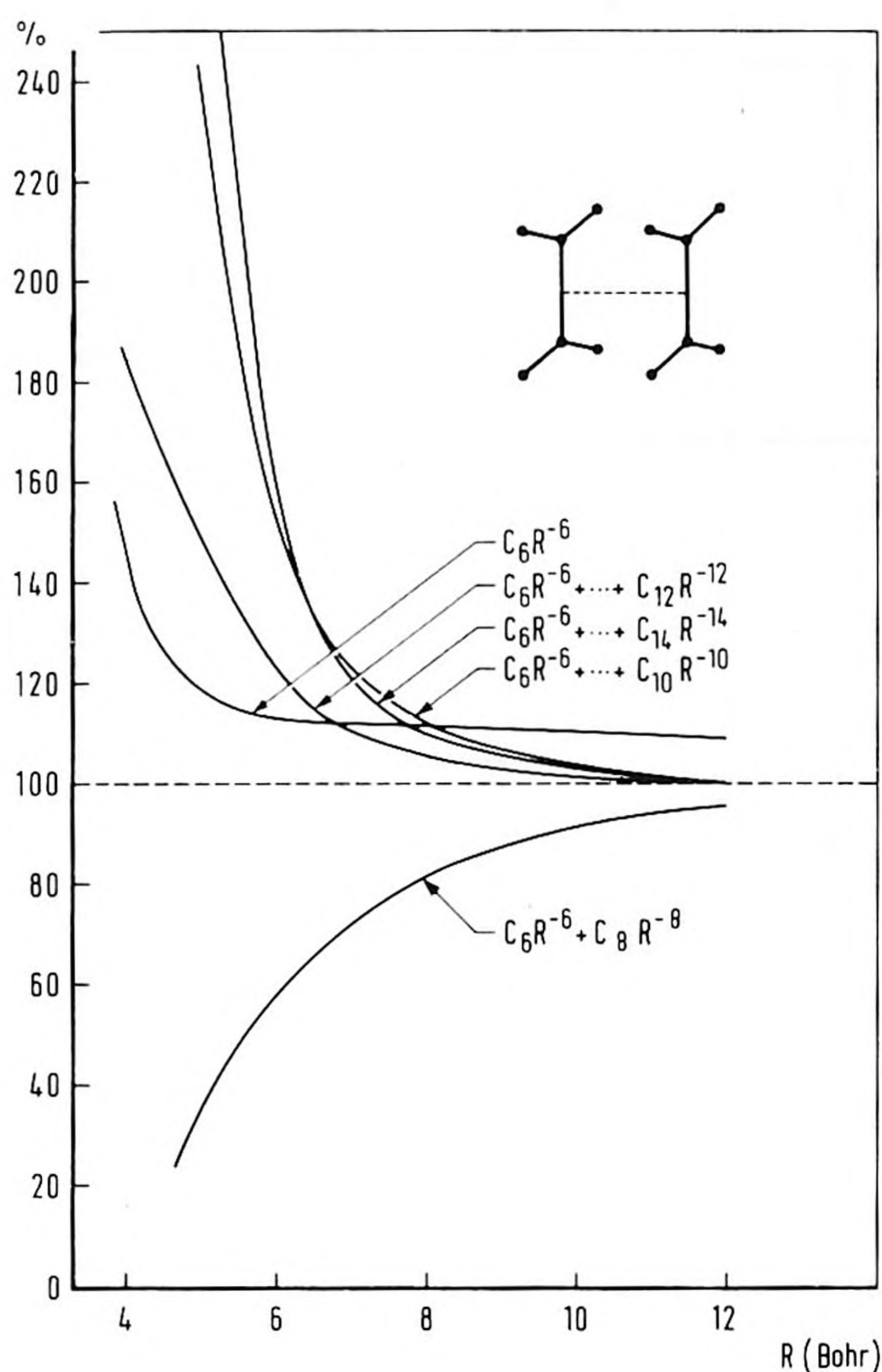
**Fig. 2.** Ratio of the multipole expanded (eqn. 16) and the unexpanded electrostatic energy (eqn. 12) for two parallel ethene molecules (from ref.<sup>75</sup>). Different multipole expansion lengths are shown

deviates from the unexpanded result, due to charge penetration. Such cases have been found for molecules also (see, for instance, fig. 4 for  $N_2-N_2$ ).

If we look specifically at the anisotropic ( $L_A, L_B \neq 0$ ) terms in the intermolecular potential, the convergence of the second order multipole expansion is slower than for the isotropic terms. This is caused by the strongly anisotropic mixed-pole ( $l \neq l'$ ) contributions, which occur in the higher dispersion and induction multipole terms but not in the first term. This is illustrated in fig. 1 for the dispersion energy in the pyrazine dimer  $(C_4N_2H_4)_2$ . Fig. 5 shows that for the  $N_2$  dimer the total anisotropy in the dispersion energy is comparable in size with the (purely anisotropic) electrostatic multipole interaction energy. The anisotropy is even stronger (relatively) in the induction energy, but the total induction energy is much smaller than the dispersion energy for the molecules we have considered:  $H_2$ ,  $N_2$ ,  $C_2H_4$ , benzene, azabenzenes, which have zero or small dipole moments.

After the long range interactions, we now consider explicitly the behaviour of the overlap (penetration, exchange) contributions to the interaction potential, particularly in the region around the Van der Waals minimum. In fig. 4 we have plotted these terms, together with the first and second order multipole interactions, as a function of distance for two parallel  $N_2$  molecules, and in fig. 5 as a function of the molecular orientation at  $R = 4 \text{ \AA}$ . (The Van der Waals minimum in the isotropic  $N_2-N_2$  potential lies at  $R = 4.1 \text{ \AA}$ <sup>136</sup>). The distance dependence is typical for closed shell molecules: with decreasing  $R$  we observe an attractive first order Coulomb interaction caused by charge penetration and a repulsive first order exchange interaction. Both increase exponentially, but the (Pauli) exchange repulsion dominates the



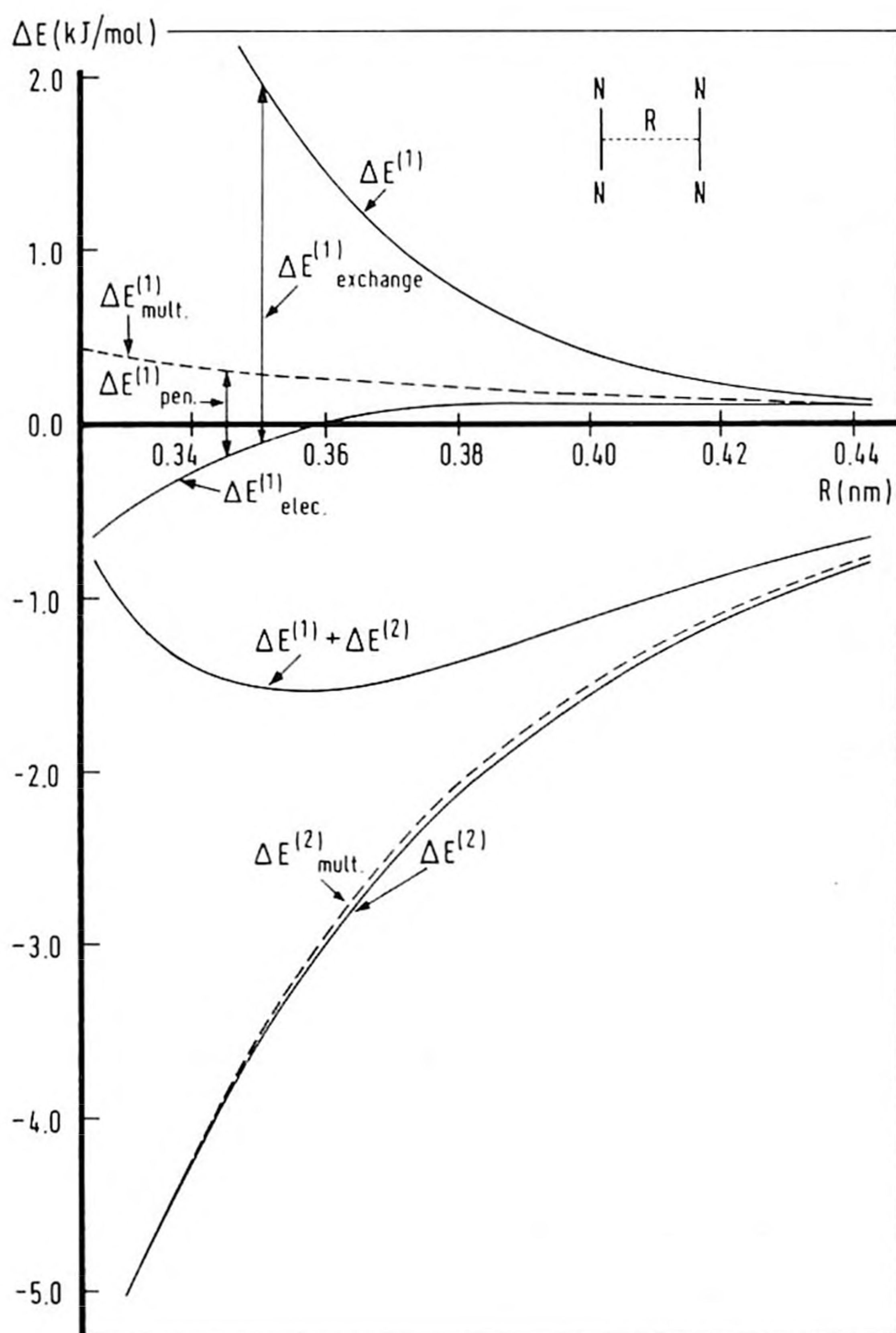


**Fig. 3.** Ratio of the multipole expanded (eqns. 20, 21) and the unexpanded dispersion and induction energy (eqn. 18) for two parallel ethene molecules (from ref.<sup>75</sup>). Different multipole expansion lengths are shown

penetration attraction by a factor of 5 to 10. The distance where these contributions begin to modify significantly the long range multipole interactions usually lies around the Van der Waals minimum: for  $N_2$  it is slightly outside this minimum (which lies, for two parallel molecules at  $R = 3.6 \text{ \AA}$ ), for  $H_2$  it is slightly inside<sup>137</sup>). This depends on the diffuseness of the electron clouds, how far they protrude from the nuclear framework, as reflected, for instance, by the sign of the molecular quadrupole moment<sup>138</sup>). In the second order (dispersion and induction) energy the overlap effects are considerably smaller than in first order. In fig. 4 we see that they happen to be practically negligible for this particular (parallel)  $N_2-N_2$  orientation; in other orientations they are somewhat larger. In fig. 5 we observe that the overlap contributions, although always repulsive, are the dominating anisotropic terms at distances around the Van der Waals minimum (or shorter). This will be reflected in the structure of the Van der Waals molecules (cf. sect. 4).

An interesting subject we may comment upon is the interaction between (planar) molecules with conjugated  $\pi$ -electron system (e.g. aromatic molecules). It is sometimes argued that these molecules show a particularly strong dispersion attraction because of the large in-plane polarizability of the  $\pi$ -electrons. In a series of ab initio calculations for benzene and several azabenzenes<sup>84,85</sup>), Mulder et al.





**Fig. 4.** Different contributions to the interaction energy between two parallel  $N_2$  molecules; ab initio results from refs<sup>101, 136</sup>.

$\Delta E_{\text{elec.}}^{(1)}$ , eqn. (12),

$\Delta E_{\text{mult.}}^{(1)}$ , eqn. (16), sum of complete  $R^{-n}$  terms for  $n = 5, 7, 9$

$\Delta E^{(1)}$ , eqn. (30)

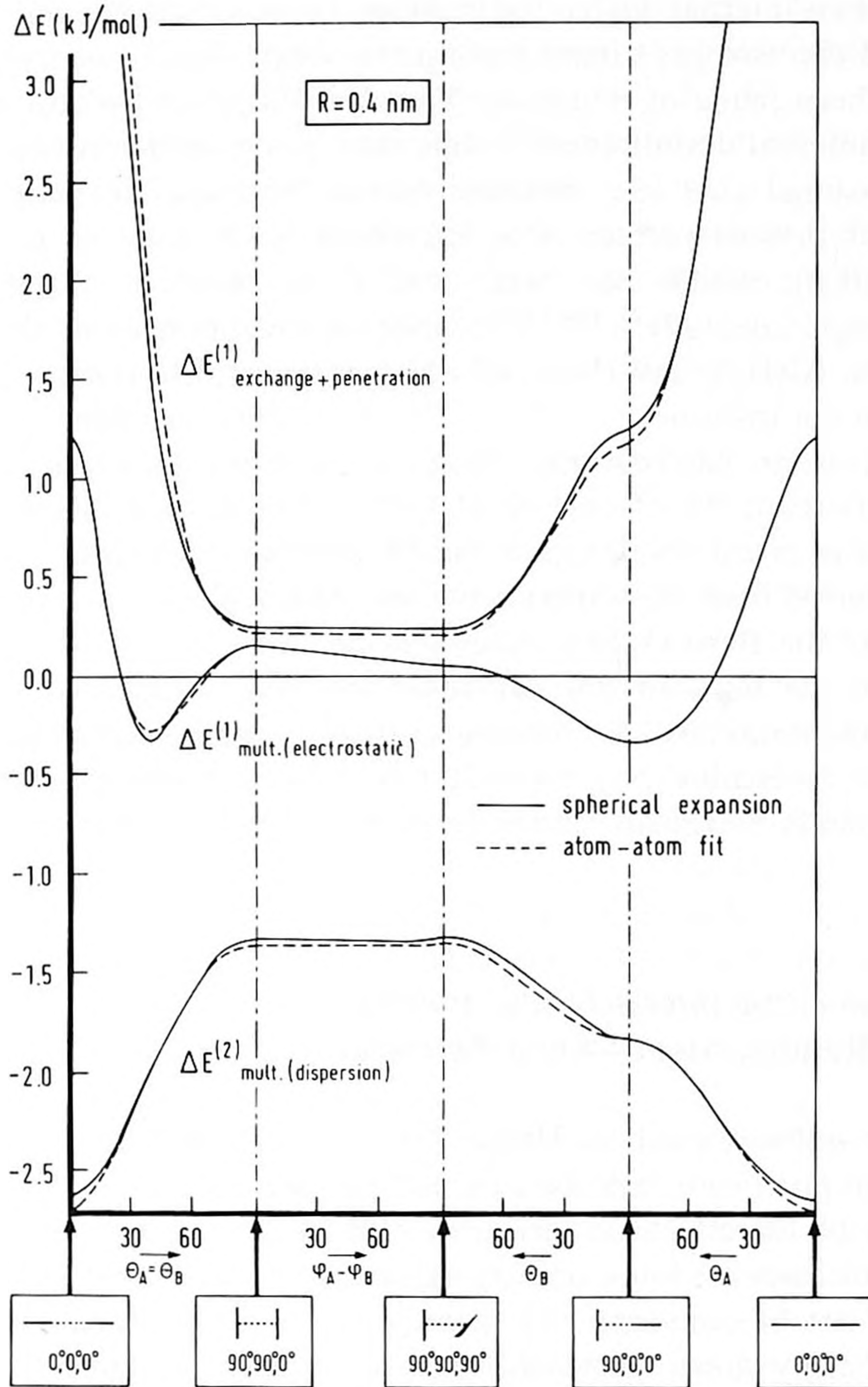
$\Delta E^{(2)} \equiv \Delta E_{\text{elec.}}^{(2)}$ , eqn. (18)

$\Delta E_{\text{mult.}}^{(2)}$ , eqn. (21), sum of complete  $R^{-n}$  terms for  $n = 6, 8, 10$

Short range penetration,  $\Delta E_{\text{pen.}}^{(1)}$ , eqn. (17), and exchange,  $\Delta E_{\text{exch.}}^{(1)}$ , eqn. (28), effects become visibly important with decreasing  $R$  (in first order)

have found however, (in contrast with earlier estimates<sup>139, 140</sup>) and semi-empirical calculations<sup>141</sup>) that also the perpendicular  $\pi$ -polarizability is far from negligible. Moreover, it appeared that for none of the polarizability components the  $\pi$ -electron contribution really dominates over the contribution from the  $\sigma$ -skeleton. Also in determining the long range dispersion coefficients the  $\pi$ -electrons are certainly not dominant (less than 23 % of  $C_6$ ) for this class of molecules<sup>85</sup>). For larger molecules (naphthalene, anthracene, etc.) the relative  $\pi$ -contribution is expected to be somewhat larger, though<sup>85</sup>).





**Fig. 5.** Orientational dependence of different long range (multipole) and short range (exchange + penetration) contributions to the  $N_2-N_2$  interaction energy, at  $R = 4 \text{ \AA}$ , from ref.<sup>136). Orientations are described by the angles  $\theta_A$ ,  $\theta_B$ ,  $\phi_A - \phi_B$ , see table 1. Curves generated by the spherical expansion(4) and by the atom-atom fit (8) of the “ab initio” potential are shown</sup>

## 4 Structure of Van der Waals Molecules

If we want to predict the structure, the stability and the vibrational and rotational spectra of Van der Waals molecules, we have to know the complete intermolecular potential as a function of the intermolecular distance(s) and the molecular orientations. For rare gas dimers<sup>31)</sup> and for some rare gas atom-diatom molecule (e.g.  $H_2$ ,  $HCl$ ) systems rather detailed information about the potential is available from experiment<sup>1, 22–27, 142, 143)</sup>, from ab initio calculations<sup>115, 124, 125, 144, 145)</sup> or both<sup>29, 30)</sup>.



The latter systems have only two internal degrees of freedom, however, (in the rigid molecule approximation) and the rare gas dimers have just a single one, of course. Some ab initio studies have been made of molecular Van der Waals (or hydrogen bonded) systems with more internal coordinates<sup>119)</sup>, but mostly they concern only specific points or one-dimensional cuts (e.g. distance curves for fixed molecular orientations) of the potential (hyper) surface. One exception is the case of the simplest molecular dimer  $(\text{H}_2)_2$ , which has been studied in detail, both ab initio<sup>116, 124, 125, 146, 147)</sup> and experimentally<sup>26, 148–154)</sup>. Another exception form the two Van der Waals molecules,  $(\text{C}_2\text{H}_4)_2$  and  $(\text{N}_2)_2$ , of which the complete potential surfaces have been obtained in our institute<sup>63, 75, 155, 101, 136)</sup> via ab initio calculations. The  $\text{N}_2\text{—N}_2$  potential, in particular, has been the subject of much previous (semi-) empirical work<sup>156)</sup>. The dimers  $(\text{N}_2)_2$ <sup>158, 159)</sup> and  $(\text{C}_2\text{H}_4)_2$ <sup>160, 161)</sup> have been investigated experimentally too, but even for  $(\text{N}_2)_2$  where the IR spectrum is known<sup>158)</sup>, the structure could not be inferred from the experiments yet. Although we have not carried out the second step in the Born-Oppenheimer scheme, the solution of the nuclear motion, we shall, on the basis of our calculated potentials, make some remarks about the equilibrium structure, the binding and the internal molecular mobility in the Van der Waals molecules  $(\text{N}_2)_2$  and  $(\text{C}_2\text{H}_4)_2$ . These remarks may be confronted with new experiments which are certainly to be expected in the near future.

#### 4.1 Analytical Representation of the Intermolecular Potential; Fitting of the Ab Initio Results; Atom—Atom Potentials

For all but the very smallest systems, (such as  $\text{HeH}_2^+$ <sup>162)</sup> and even there it is very expensive), it is not possible in practice to calculate the full potential surface, with a grid fine enough that it can be directly used for solving the (nuclear) dynamical problem in Van der Waals molecules (or for scattering calculations). Moreover, such a numerical potential would not be convenient for most purposes. Therefore, one usually represents the potential by some analytical form, for instance, a truncated spherical expansion (1) or another type of model potential (cf. sect. 2). The parameters in this model potential can be obtained by fitting the ab initio results for a limited set of intermolecular distances and molecular orientations. Since we have encountered some difficulties in this fitting procedure which we expect to be typical, we shall describe our experience with the  $(\text{C}_2\text{H}_4)_2$  and  $(\text{N}_2)_2$  cases in some detail. At the same time, we use the opportunity to make a few comments about the convergence of the spherical expansion used for  $(\text{N}_2)_2$  and about the validity of the atom-atom model potential applied to both  $(\text{C}_2\text{H}_4)_2$  and  $(\text{N}_2)_2$ .

##### 4.1.1 $(\text{C}_2\text{H}_4)_2$

For this dimer the interaction potential has been calculated<sup>155, 75)</sup> for 8 different orientations of the two molecules, for 3 distances around  $R = 4.8 \text{ \AA}$  ( $9a_0$ ) including (first order) exchange and penetration effects and for 8 distances from  $R = 6.4$  to  $10.6 \text{ \AA}$  (12 to  $20a_0$ ) in the multipole expansion. Second order overlap effects



(penetration and exchange) were neglected. The number of orientations (8) is far too small (the system has 6 internal coordinates, 1 distance and 5 angles, and it needs all 5 quantum numbers,  $L_A$ ,  $K_A$ ,  $L_B$ ,  $K_B$ ,  $L$ , to qualify its angular functions (1 b)) to make a spherical expansion (1) of the interaction potential, even if one assumes that this expansion could be truncated after  $L_A, L_B = 2$  terms. Some simplified model potential had to be adopted in order to reduce the number of fitting parameters. Wasiutynski et al.<sup>155)</sup> have chosen an atom-atom potential (of the exp-6-1 type):

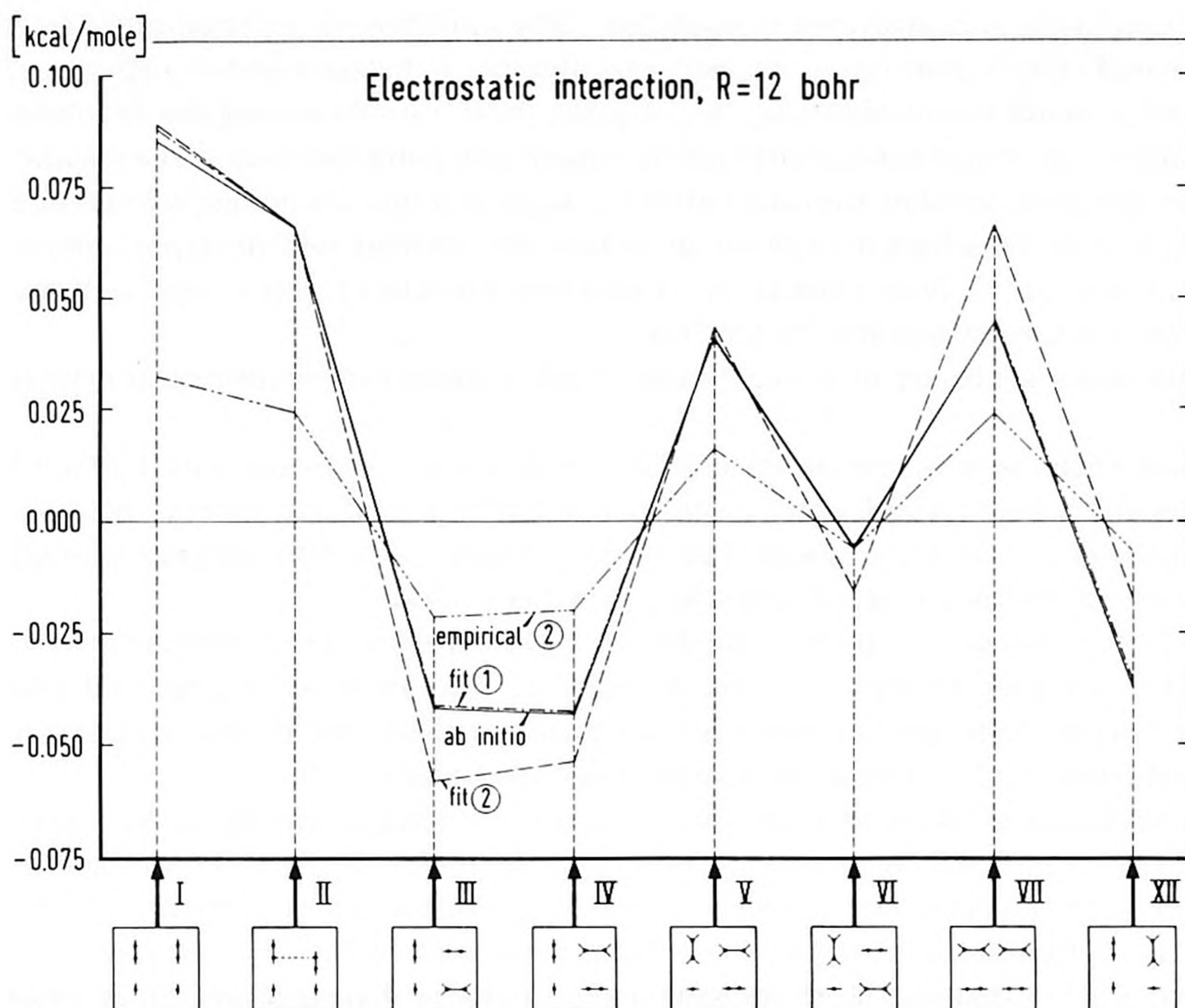
1. because it has relatively few parameters,
2. because it is easy to use in lattice dynamics calculations for the molecular crystal, and
3. because there is a considerable amount of work on hydrocarbons based on empirically parametrized atom-atom potentials<sup>163-166)</sup> (from crystal heats of sublimation and structural data). The ab initio results could be used to check both the atom-atom model and its empirical parametrization.

At first, it was tried to optimize all the atom-atom parameters simultaneously by a best fit to the total ab initio interaction energies, but this procedure led to highly correlated fit parameters with no well-defined optimum. Then, the ab initio interaction energy was separated and three independent fits were made:

- (i) the electrostatic (multipole) interaction energy (16) calculated up to  $R^{-7}$  terms inclusive was fitted by an atomic point charge model. If the point charges are fixed on the nuclei (which leads to a single independent charge parameter for the  $C_2H_4$  molecule) the fit is bad (root mean square deviation 23 %) especially for some  $C_2H_4$  orientations. If we extend the model to 4 parameters by allowing the charges to shift away from the nuclei the fit is much better (r.m.s.d. 3.6 %).
- (ii) the dispersion (multipole) energy (21) truncated after  $R^{-8}$  terms was fitted by an  $r^{-6}$  atom-atom potential. This went quite well (surprisingly well, if we consider the incorrect asymptotic angular behaviour of the  $r^{-6}$  atom-atom potential<sup>37, 167)</sup>), but an averaging constraint had to be imposed on the C—H parameter, in order to avoid high correlation. The final fit, with only two independent parameters, had a r.m.s.d. of 7.1 %. The induction energy, which is very small relative to the dispersion energy, was neglected.
- (iii) the overlap (first order penetration and exchange) energy, (17) and (28) calculated from (30), was fitted by an exponential atom-atom potential. The electrostatic penetration energy was separated from the electrostatic multipole energy (i), since the atom-atom (point charge) model cannot account for penetration effects. It was added to the exchange energy which has about the same exponential distance dependence. It is this distance dependence, which was actually found in ab initio calculations<sup>145, 155, 168)</sup>, that justifies the use of an exponential atom-atom repulsion, rather than an  $r^{-n}$  type. Just as in (ii) one had to put averaging constraints on the C—H parameters and, moreover, the H—H repulsion parameters had to be determined by comparing specific dimer geometries where the energy differences are mainly caused by H—H contacts. The final fit (with 4 independent parameters) is still rather unsatisfactory (r.m.s.d. 33 %).

The different contributions to the interaction potential are displayed in figs 6, 7 and 8, for 8 different orientations of the  $C_2H_4$  molecules in the dimer. These figures clearly illustrate the quality of the atom-atom model in representing the orientational de-





**Fig. 6.** Electrostatic multipole expanded interaction energy between two ethene molecules for 8 different orientations at  $R = 12a_0$  (ab initio results from refs.<sup>75,155</sup>). Fits ① and ② are atom-atom (point charge) model fits to the ab initio data; ① is a fit with the charges shifted from the nuclei, ② has the charges fixed on the nuclei. Also indicated is an empirical atom-atom potential; for details see ref.<sup>155</sup>

pendence of the interaction potentials; they also contain some empirical atom-atom potentials for comparison.

We can draw the following conclusions. For the dispersion (multipole) interaction energies the atom-atom model works reasonably in the  $(C_2H_4)_2$  case, (and in other cases, too: benzene, azabenzenes<sup>167</sup>). Also the electrostatic (multipole) energy can be well represented by an atom-atom (point charge) model, if the point charges are allowed to shift away from the nuclei, (or if one adds extra point charges<sup>169</sup>). For the overlap energy the deviations from the ab initio results are much stronger. This might be due to deviations from pairwise additivity (cf. sect. (2), the intra-molecular overlap between the atomic orbitals is considerable,  $\approx 0.5$ ). But also it can be caused partly by the anisotropy of the atom-atom interactions. Both effects are related to the chemical bonding within the molecules which is ignored in the atom-atom model. Actually, one can observe from the ab initio results<sup>155</sup> that the C—C overlap repulsion has a longer range (corresponding to a smaller negative exponent) in the direction perpendicular to the  $C_2H_4$  plane than in the other directions. This is due to the relative diffuseness of the  $\pi$ -clouds. Fortunately, a deviation of 33% in the overlap energy does not have such a drastic effect on the potential surface as it may



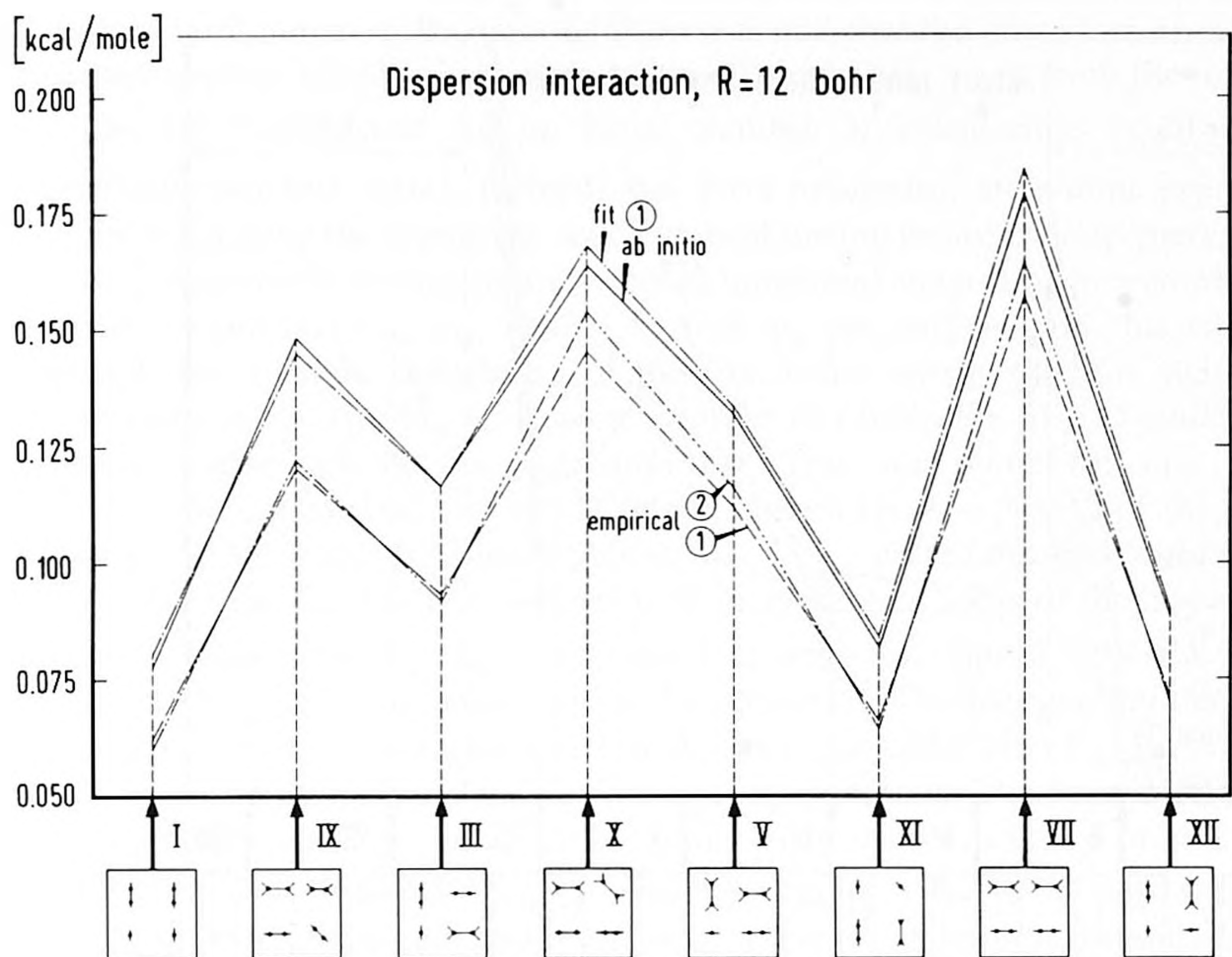


Fig. 7. Dispersion multipole interaction energy between two ethene molecules for 8 different orientations at  $R = 12a_0$  (ab initio results from refs.<sup>75, 155</sup>). Fit ① is an atom-atom fit to the ab initio data. Also indicated are two empirical atom-atom potentials; for details see ref.<sup>155</sup>

seem. The overlap repulsion depends very steeply on the intermolecular distance. A large deviation in the repulsive energy will cause a much smaller change in the equilibrium distance and not too much of a change in the depth of the Van der Waals well.

The atom-atom potential fitted to the ab initio data gives fairly realistic results<sup>155</sup> for the equilibrium structure<sup>170</sup> (unit cell parameters and molecular orientations in the cell), the cohesion energy<sup>171</sup> and the phonon frequencies of the  $C_2H_4$  molecular crystal. The latter have been obtained via both a harmonic and a self-consistent phonon lattice dynamics calculation<sup>155, 172</sup> and they were compared with IR<sup>173</sup> and Raman<sup>174</sup> spectra. About some of the empirical hydrocarbon atom-atom potentials<sup>164</sup>, which are fitted to the crystal data, we can say that they correspond reasonably well with the ab initio results (see figs. 6, 7, 8), their main defect being an underestimate of the electrostatic multipole-multipole interactions.

#### 4.1.2 $(N_2)_2$

In this system the long range (multipole) interaction energy has been calculated<sup>101</sup> directly in the form of a spherical expansion (4): electrostatic  $R^{-5}$ ,  $R^{-7}$  and  $R^{-9}$  terms, formula (16), dispersion  $R^{-6}$ ,  $R^{-8}$ ,  $R^{-10}$  terms, formula (21) and induction  $R^{-8}$ ,  $R^{-10}$  terms, formula (20). The multipole moments used in the electrostatic energy



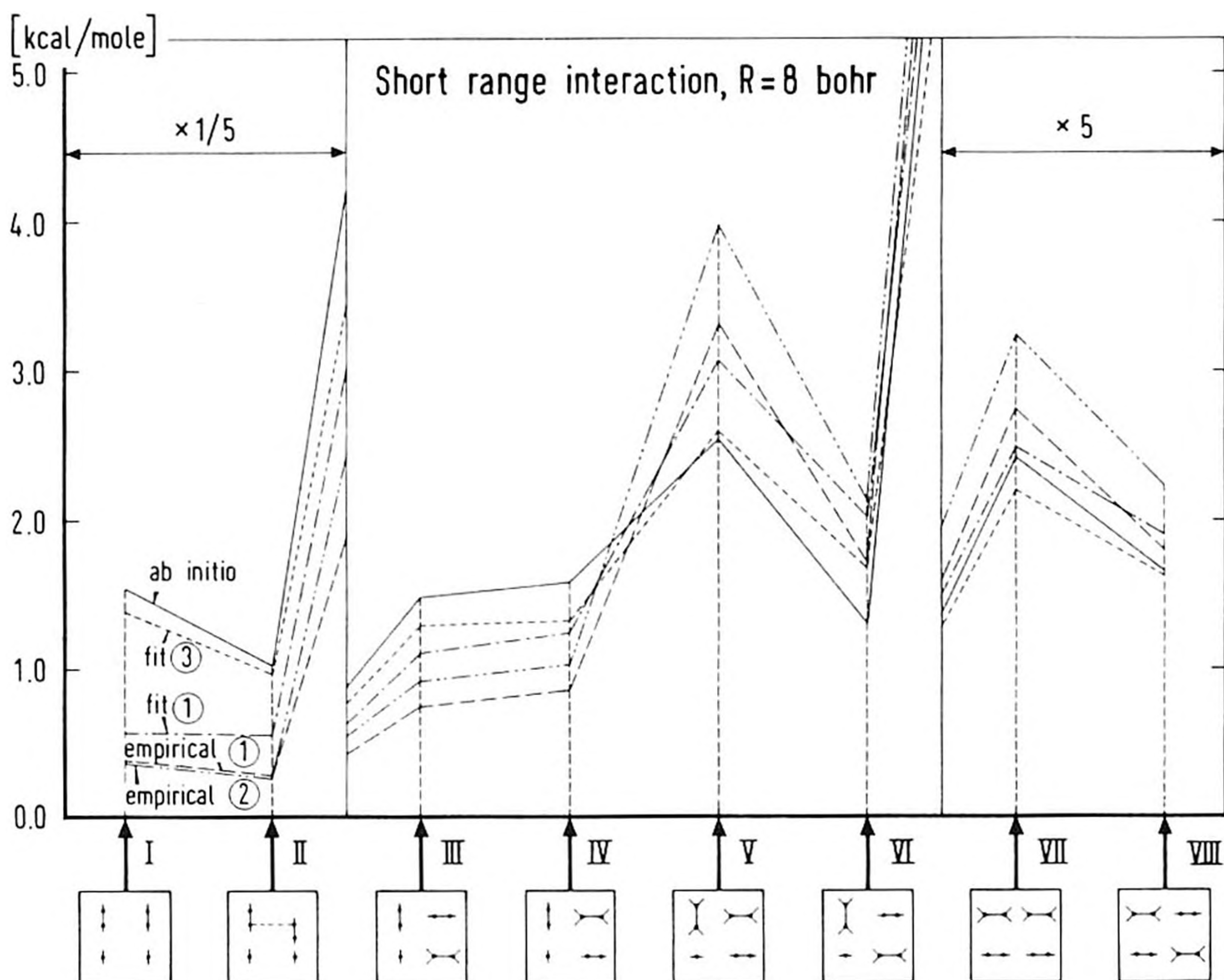


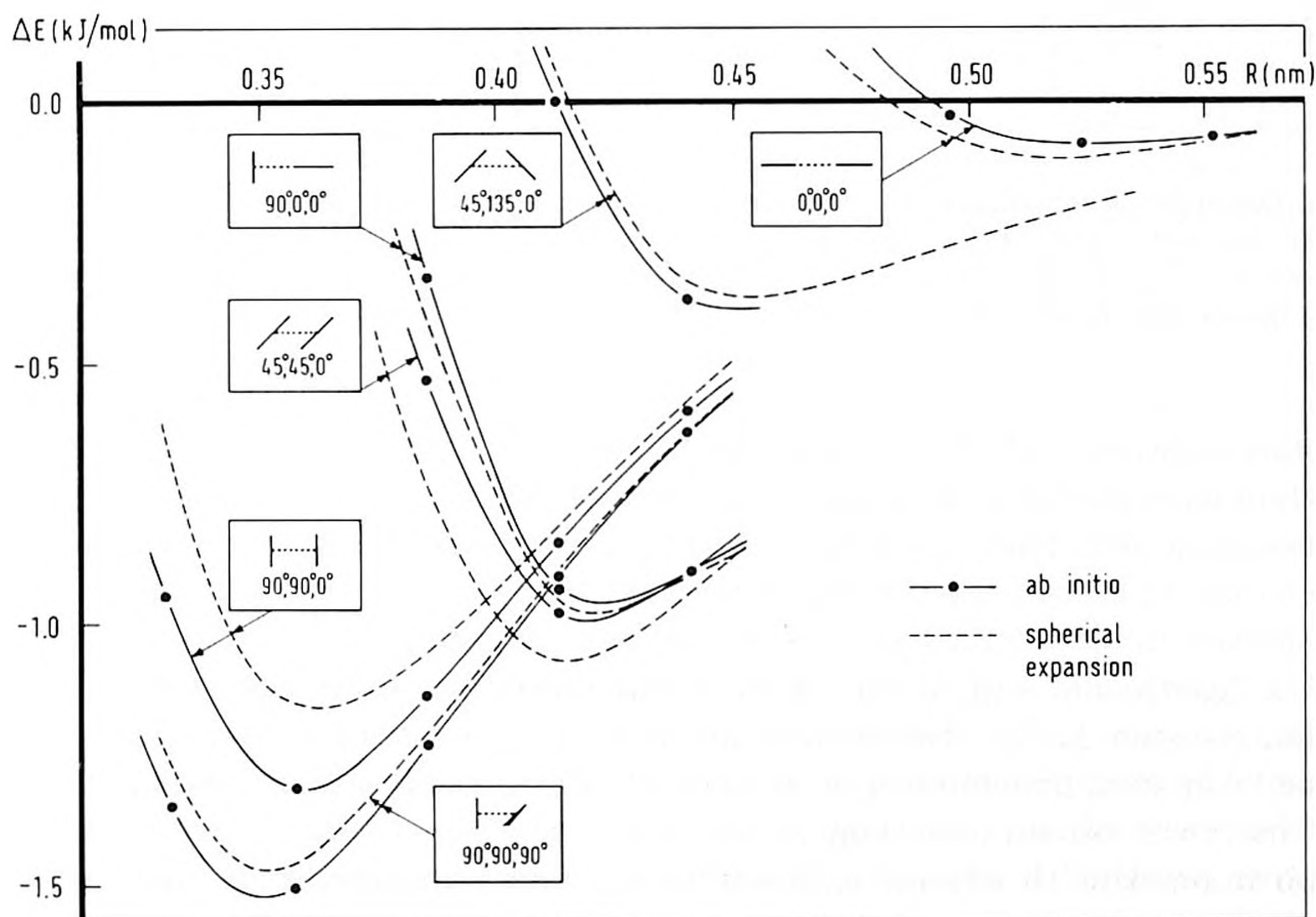
Fig. 8. Short range (exchange + penetration) interaction energy between two ethene molecules for 8 different orientations at  $R = 8a_0$  (ab initio results from ref.<sup>155</sup>). Fits ① and ③ are atom—atom fits to the ab initio data, with and without constraints for the C—H parameters. Also indicated are two empirical atom—atom potentials; for details see ref.<sup>155</sup>

agree rather well with the experimental data available, but the calculated dispersion coefficient  $C_6$  is considerably larger (25 %) than the accurate semi-empirical value<sup>95</sup>). Also the anisotropy in  $C_6$  and in the dipole polarizability  $\alpha$  are somewhat overestimated with respect to experiment. We believe this to be due to the use of Hartree-Fock wave functions for the  $N_2$  monomers (the AO basis was sufficiently large and flexible). Employing the accurate semi-empirical data for  $C_6$  and  $\alpha$  in combination with the ab initio results, better estimates are given for the dispersion coefficients  $C_6$ ,  $C_8$ ,  $C_{10}$  and their anisotropic components<sup>101</sup>). We shall refer to these values as “ab initio”. The induction energy is very small and can be neglected relative to the dispersion energy just as for  $(C_2H_4)_2$ .

In first instance, the overlap (penetration and exchange) energy has been computed (in first order, from expression (30)) for 6 different orientations of the two  $N_2$  molecules and 5 distances<sup>136</sup>). Also the second order penetration contribution (25) was computed (for 10 of the 30 dimer geometries), but this contribution is small relative to the first order penetration contribution and it has been neglected. In principle, these ab initio data should be sufficient to calculate (for each  $R$ ) 6 coefficients  $\Delta E_{L_A, L_B, L}(R)$  in the spherical expansion (4). Alternatively one can obtain all (independent) terms up to  $L_A, L_B = 2$ , i.e.  $(L_A, L_B, L) = (0, 0, 0), (2, 0, 2), (2, 2, 0), (2, 2, 2), (2, 2, 4)$ , from the data for 5 orientations and use the 6<sup>th</sup> orientation for a check on the truncation error. The results of this procedure were completely

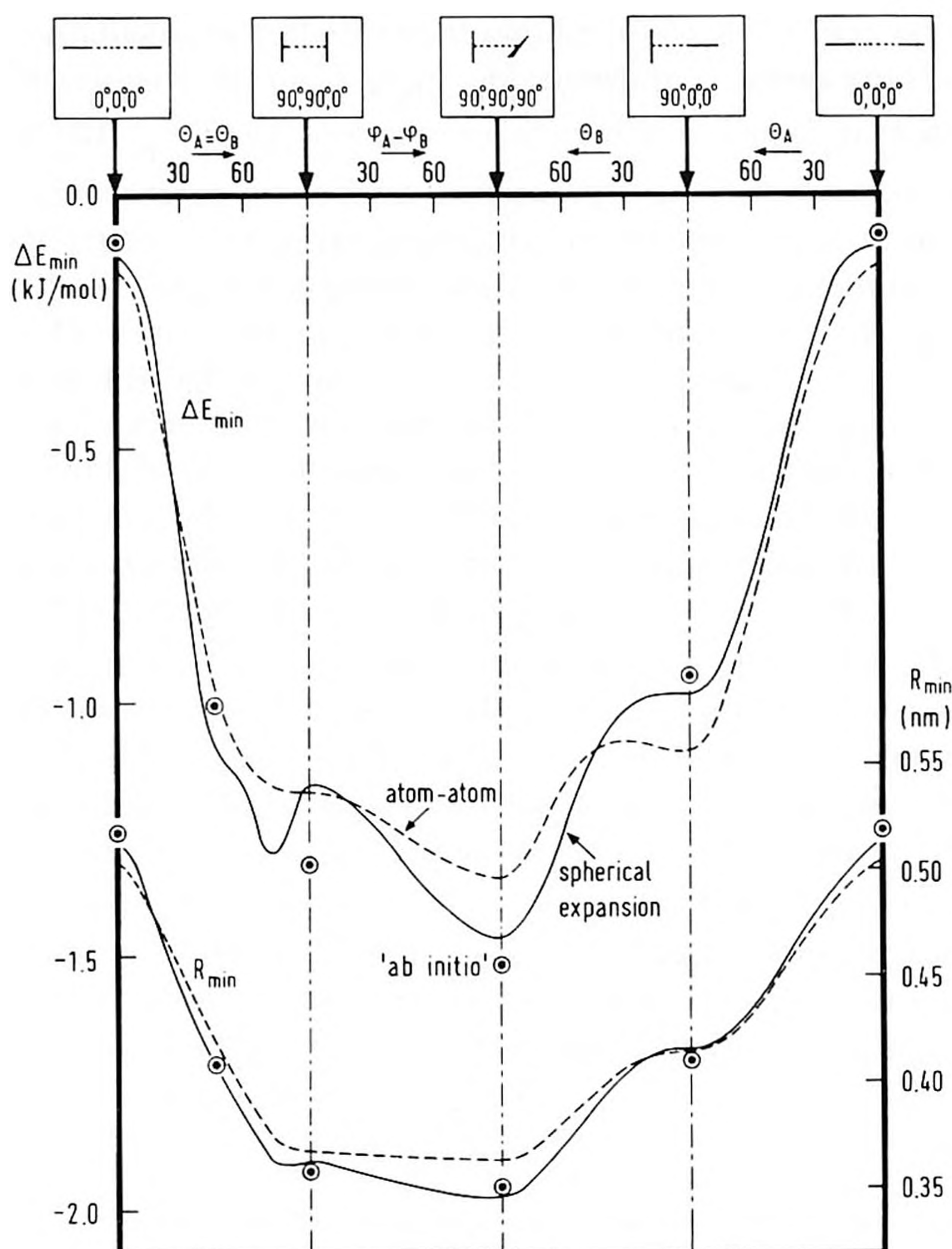


unsatisfactory, however. Berns et al.<sup>136)</sup> have found that the procedure of calculating a certain number of spherical expansion coefficients  $\Delta E_{L_A, L_B, L}$  from the interaction energies  $\Delta E^{AB}$  computed for an equal number of orientations ( $\omega_A, \omega_B, \Omega$ ) is numerically not very stable. Instead, they have proceeded, after some experimentation, by calculating the expansion coefficients of the (ab initio) overlap energy directly from expression (10), using a suitably chosen numerical integration procedure over the angular coordinates  $\omega_A, \omega_B, \Omega$  ( $\theta_A, \theta_B$  and  $\phi_A$  are sufficient in this case). This involved the ab initio calculation of the first order energy (30) for 105 different orientations of the two  $N_2$  molecules, in order to obtain the first 18 (independent) dynamic coefficients in the expansion (4). This was done for one distance,  $R = 3 \text{ \AA}$ , well inside the Van der Waals minimum (at  $R = 4.1 \text{ \AA}$ ) of the isotropic potential. It was found that the coefficients  $\Delta E_{L_A, L_B, L}$  indeed decrease with increasing  $L_A, L_B$ ; for fixed  $L_A, L_B$  they increase with increasing  $L$ . Some of the highest coefficients calculated (for  $L_A, L_B = 4, 4$  and  $6, 2$ ) were less than 1% of the isotropic coefficient  $\Delta E_{0,0,0}$ . It can be concluded that the series (4) converges, but that some of the higher terms are still important. Truncation of the series after  $L_A, L_B = 2, 2$  leads to an error of 16%, truncation after  $L_A, L_B = 4, 4$  to 2% error. Next, it was decided, on the basis of the ab initio results for 6 distances and 6 orientations, to represent all the coefficients  $\Delta E_{L_A, L_B, L}(R)$  up to  $L_A, L_B = 6, 2$  by the same exponential function of  $R$ . This caused a somewhat larger error (7%), but it is certainly not a bad (first) approximation. The results, in combination with the long range results, yield a reasonable fit of the calculated  $N_2-N_2$  interaction potential (see figs. 9 and 10).



**Fig. 9.** Total interaction energy between two  $N_2$  molecules at 6 different orientations, described by the angles  $\theta_A, \theta_B, \phi_A$ . "Ab initio" results and spherical expansion (4) of these results from ref.<sup>136)</sup>





**Fig. 10.** Orientational dependence of the Van der Waals minimum in the  $\text{N}_2\text{--N}_2$  interaction potential. The well depth  $\Delta E_{\min}$  and equilibrium distance  $R_{\min}$  were obtained by varying  $R$  for each orientation  $\theta_A$ ,  $\theta_B$ ,  $\phi_A$  ( $\phi_B = 0$ ). “Ab initio” results, spherical expansion (4) and atom-atom fit (8) of these results from ref.<sup>136)</sup>

Another approach, which was taken by Berns et al.<sup>136)</sup> was to fit the “ab initio” interaction energies (for 6 distances and 6 orientations) by an atom-atom potential. This was again done term by term, just as for  $(\text{C}_2\text{H}_4)_2$ . The electrostatic (multipole) energy (i) was fitted by a 3 parameter axial point charge model; average error 6.5%. The dispersion (multipole) energy (ii) was fitted by a 2 parameter  $r^{-6}$  potential; average error 6.3% (including a slight shift of the origin away from the nuclei; without this shift the error was 9.7%). The overlap (penetration and exchange) energy (iii) was represented by an exponential atom-atom repulsion with 2 parameters (the optimum origins lie practically on the nuclei, in this case); average error 9.2%. The resulting atom-atom potential<sup>136)</sup> appears to describe the angular dependence of the  $\text{N}_2\text{--N}_2$  “ab initio” potential surprisingly well (see figs. 5 and 10), also for the 105 orientations calculated (at  $R = 3 \text{ \AA}$ ). It is striking that the atom-atom model works much better for  $\text{N}_2\text{--N}_2$  than for  $\text{C}_2\text{H}_4\text{--C}_2\text{H}_4$ , especially for the overlap energy. Maybe this is due to the lone-pair electrons in  $\text{N}_2$  balancing the effects of chemical bonding. The



properties of the  $N_2$  crystal  $\alpha$  and  $\gamma$  phases<sup>156, 157)</sup> (equilibrium structure, cohesion energy, phonon frequencies) are very well described<sup>136, 175)</sup> by this atom-atom potential.

## 4.2 Potential Surfaces of Van der Waals Molecules; $(N_2)_2$ and $(C_2H_4)_2$

We have studied the potential hypersurfaces for the Van der Waals dimers  $(N_2)_2$  and  $(C_2H_4)_2$  by varying all the independent internal coordinates (in the rigid molecule approximation, 3 angles for  $(N_2)_2$ , 5 angles for  $(C_2H_4)_2$  and the distance  $R$  in both cases). It is of course not possible to present the complete surfaces pictorially; we have displayed in figs. 9 and 10 some typical cuts through the surface of  $(N_2)_2$ . Especially fig. 10 contains much information since the distance was varied to find the energy minimum  $\Delta E_{\min.}$  for each orientation  $(\theta_A, \theta_B, \phi_A)$ . In the figs. 4 and 5 and 6, 7 and 8 the different contributions ("long range" (i) and (ii) and "short range" (iii), see the previous paragraph) to the interaction energy are plotted. It is not possible to indicate very pronounced minima in the surfaces. For  $(N_2)_2$  we have found one absolute minimum at  $\Delta E_{\min.} = 1.5$  kJ/mol in the crossed structure  $\theta_A = \theta_B = \phi_A = 90^\circ$ ,  $R = 3.5$  Å; for  $(C_2H_4)_2$  we have found two equally deep minima at  $\Delta E_{\min.} = 5.0$  kJ/mol, one for a staggered parallel structure with  $R = 3.93$  Å the other for a skew structure with  $R = 3.87$  Å (see table 4). The potential surfaces are rather flat around these minima, however, and many other possible structures exist with a binding energy higher than 80% of  $\Delta E_{\min.}$ . Therefore, we expect the  $N_2$  and  $C_2H_4$  molecules in the dimers to make rather wide angular oscillations (librations) in some directions. For instance, the barrier for a complete rotation over  $\phi_A$  in the  $N_2$  dimer with  $\theta_A = \theta_B = 90^\circ$  is about 0.2 kJ/mol (13% of  $\Delta E_{\min.}$ ) with practically no variation of the equilibrium distance (see fig. 10) (the rotational constant of free  $N_2$  is  $2.0 \text{ cm}^{-1} = 0.024$  kJ/mol). At somewhat higher temperatures where the dimer is still stable, (in some cases maybe at zero temperatures already) these oscillations will go over into (weakly) hindered rotations. In other directions, rotations of the molecules are strongly hindered; the dimer must almost dissociate before such a rotation becomes possible. (e.g. the rotations through the orientation  $\theta_A = \theta_B = \phi_A = 0^\circ$  in the  $N_2$  dimer, fig. 10). The solution of the dynamical problem for the nuclei may be not an easy job. Neither the model of almost free rotors, which works very well for the  $(H_2)_2$  case<sup>154)</sup>, nor the harmonic (or weakly anharmonic) oscillator model, which works reasonably well in molecular crystals, may be applicable. In this sense, the problem is comparable to that of the plastic phases in molecular crystals, such as the  $\beta$ -phase of solid  $N_2$ .

Leaving aside this dynamical problem, we can make some further remarks about the equilibrium structure of Van der Waals molecules. Some attempts have been made to predict this structure from the molecular properties, multipole moments, polarizabilities, which are reflected in the long range interactions (electrostatic, dispersion). Other authors<sup>161, 176)</sup> have assumed that the equilibrium structure of Van der Waals dimers resembles the structure of nearest neighbour pairs in molecular crystals. The latter approach could possibly be justified by packing considerations (short range repulsion). An example of the first approach is the prediction of a T-shaped ( $\theta_A = 90^\circ$ ,  $\theta_B = \phi_A = 0^\circ$ ) equilibrium structure for the  $N_2$ -dimer, mainly



**Table 4a.** Most stable dimer structures:  $\text{N}_2\text{—N}_2$ 

	R (Å)	$\theta_A^a$	$\theta_B^a$	$\phi_A^a$	$\Delta E$ (kJ/mol)
dimer <sup>b</sup>	3.64	90°	90°	90°	1.35
$\alpha\text{—N}_2$ crystal <sup>c</sup> neighbour pair	3.99 (4.04 <sup>d</sup> )	90°	35°	55°	1.05
$\gamma\text{—N}_2$ crystal <sup>c</sup> neighbour pair	3.79 (3.98 <sup>d</sup> )	90°	42°	90°	0.94

<sup>a</sup> Angular coordinate system with  $\Theta = \Phi = \phi_B = 0^\circ$ , see table 1

<sup>b</sup> Minimum in the potential energy surface, neglecting the effects of nuclear motion. Full minimum search was done with the atom—atom potential, fitted to the “ab initio” results<sup>136)</sup>

<sup>c</sup> Experimental crystal structures, see ref.<sup>156)</sup>,  $\Delta E$  calculated with the atom—atom potential<sup>136)</sup>

<sup>d</sup>  $R_{\min.}$  obtained with the atom—atom potential<sup>136)</sup> for fixed (crystal) orientations

on the basis of attractive quadrupole-quadrupole interactions<sup>158)</sup>. Addition of the anisotropic dispersion interactions<sup>101)</sup> and, even, of the short range repulsion in an approximate model<sup>177)</sup> gives further support for the stability of this T-shaped  $\text{N}_2\text{—N}_2$  structure, but this also suggests another possible structure of equal stability, the staggered parallel one ( $\theta_A = \theta_B \simeq 45^\circ$ ,  $\phi_A = 0^\circ$ ). A related approximate model which includes the short range repulsions<sup>178)</sup> leads to different predictions, however. Now that we have calculated both the (anisotropic) long range and short range contributions more quantitatively, we can make some more definite, although not final, statements on this matter.

In fig. 5 we see that, indeed, the T-shaped and the staggered parallel structure have maximum electrostatic attraction. The dispersion energy is most favourable, of course, for the linear structure. For distances in the neighbourhood of the (isotropic) Van der Waals minimum the (short range) exchange repulsion is the dominant anisotropic term, however. Since it increases very steeply when the molecular charge clouds start to overlap (especially in the linear structure  $\theta_A = \theta_B = \phi_A = 0^\circ$ ), it determines to a large extent the distance of closest approach of the molecules. If, for a given orientation the long range interactions are not maximally attractive (when compared with other orientations, for equal distance  $R$ ), but the molecules can approach each other closely, the Van der Waals well may still be relatively deep. This is, for instance, what happens for the crossed structure ( $\theta_A = \theta_B = \phi_A = 90^\circ$ ) of the  $\text{N}_2$ -dimer. In general, one can observe this role of the short range repulsion from fig. 10, where the well depth  $\Delta E_{\min.}$  shows a strong (negative) correlation with the equilibrium distance  $R_{\min.}$ . The same phenomenon has been found for the  $\text{C}_2\text{H}_4$ -dimer: maximum binding energy (table 4) occurs for the dimer structures with the smallest  $R_{\min.}$ . Only when the short range repulsion is not very sensitive to a change of orientation (for instance, the rotation over  $\phi_A$  in the  $\text{N}_2$ -dimer with  $\theta_A = \theta_B = 90^\circ$ , see fig. 5), the long range interactions (in this case, the electrostatic interactions, even though they are repulsive) can still be important in determining the equilibrium structure.

This crucial role of the short range repulsions (closest packing) for the dimer structure may suggest that the structure of nearest neighbour pairs in the molecular



**Table 4b.** Most stable dimer structures;  $C_2H_4-C_2H_4$ 

	R (Å)	$\Theta^a$	$\Phi^a$	$\alpha_B^a$	$\beta_B^a$	$\gamma_B^a$	$\Delta E$ (kJ/mol)
dimer <sup>b</sup>	3.93	49°	27°	0°	0°	0°	5.01
dimer <sup>b</sup>	3.87	56°	14°	-59°	45°	-59°	5.05
$C_2H_4$ crystal <sup>c</sup>							
1 <sup>st</sup> neighbour pair	4.07 (4.07 <sup>d</sup> )	61°	13°	0°	0°	0°	3.89
$C_2H_4$ crystal <sup>c</sup>							
2 <sup>nd</sup> neighbour pair	4.44 (4.50 <sup>d</sup> )	54°	7°	-47°	96°	47°	2.52

<sup>a</sup> Angular coordinate system with  $\alpha_A = \beta_A = \gamma_A = 0^\circ$ ;  $\alpha_B, \beta_B, \gamma_B$  Euler angles as defined in ref.<sup>18)</sup>; molecular axes: C—C = y-axis,  $C_2H_4$ -plane = xy-plane

<sup>b</sup> Lowest minima in the atom—atom potential energy surface, fitted to the ab initio results<sup>155)</sup>

<sup>c</sup> Experimental crystal structure from ref.<sup>170)</sup>,  $\Delta E$  calculated with the atom—atom potential<sup>155)</sup>

<sup>d</sup>  $R_{min.}$  obtained with the atom—atom potential<sup>155)</sup> for the fixed (crystal) orientations.

crystal indeed forms a good indication for the structure of the Van der Waals dimer. This is supported by one of the stablest  $C_2H_4$  dimers, the one with the staggered parallel structure, which resembles rather closely one of the neighbour pairs in the crystal. The other most stable  $C_2H_4$  dimer and, also, the crossed  $N_2$  dimer deviate more strongly from the crystal neighbour configurations, however (see table 4). And, in fact, it is not obvious, even if only packing considerations determine the structure, that the optimum packing in a crystal where each molecule is surrounded by several neighbours must correspond with optimally packed dimers. The crystal neighbours should not have too unfavorable pair energies, though, and we have checked on our  $(C_2H_4)_2$  and  $(N_2)_2$  potential surfaces that this is not the case (see table 4).

Summarizing this section on the potential surfaces of  $(N_2)_2$  and  $(C_2H_4)_2$  we try to make a few concluding remarks which may be more generally applicable. Clearly, this generalization, if valid at all, is restricted to Van der Waals complexes composed of molecules which have zero or small dipole moments (excluding, for instance, hydrogen bonded systems), where the dispersion energy is the dominant cohesive contribution. Sometimes, these complexes have been called Van der Waals molecules in the proper sense. We expect the  $N_2$  and  $C_2H_4$  dimers to be typical examples of such complexes. The equilibrium structure is, in first instance, determined by minimal short range repulsions (packing, steric hindrance considerations). If these allow several rather closely packed structures with little differences in energy, then the long range anisotropic interactions (both electrostatic and dispersion) will determine the lowest energy configuration. The balance between the different attractive and repulsive contributions can be very subtle, however, and there may be several competing dimer configurations with almost equal binding energies. (Such as we have found both for  $(N_2)_2$  and for  $(C_2H_4)_2$ .) It becomes very hard then to predict the stablest structure, even on the basis of ab initio calculations. (More approximate model calculations are completely useless in this respect). Moreover, one has to take into account the (nuclear) dynamical problem. Only in combination with experimental information the calculations may provide conclusive answers about the structure of Van der Waals complexes. For instance, the technique of molecular beam deflection<sup>159)</sup>



is sensitive to the dipole moment of a Van der Waals molecule (cf. sect. 5). One of the calculated stablest structures of the  $C_2H_4$  dimer, the staggered parallel one, has a vanishing dipole moment because of symmetry. For the skew structure this is not the case. So, the experiment, if it is sufficiently sensitive, could discriminate between these structures. For the  $N_2$  dimer the stablest structure we have calculated, the crossed one, has zero dipole moment, but so has the staggered parallel one, which we find only slightly higher in energy. Here, the absence of a dipole moment is not sufficient to decide which structure is more favourable and additional experimental information is needed to check our result. On the other hand, the experimental data alone are mostly not sufficient to obtain a detailed potential surface for Van der Waals molecules; the ab initio results, wherever they can be obtained, are very helpful for interpreting the experimental observations.

## 5 Some Properties of Van der Waals Molecules

### 5.1 Orientational Dependence

In the very same way as the Born-Oppenheimer approximation allows the definition of a potential energy surface for a Van der Waals molecule, it enables, too, the concept of an interaction tensor field. This is a field dependent on the relative coordinates of the monomers and transforming as a tensor under rotation of the complex as a whole. (The potential energy surface is an example of a rank zero interaction tensor field). In the case of tensor fields it is also convenient to base the theory on irreducible tensors and to use an expansion in terms of a complete set of functions of the five angular coordinates describing a Van der Waals dimer.

The generalization of the scalar-valued angular functions (1 b) to arbitrary rank  $J$  is:

$$A_{\Lambda, N}^J(\underline{\omega}_A, \underline{\omega}_B, \vec{R}) = \sum_{M_A, M_B, M} (L_A, M_A; L_B, M_B; L, M | J, N) \times D_{M_A, K_A}^{L_A}(\underline{\omega}_A)^* D_{M_B, K_B}^{L_B}(\underline{\omega}_B)^* C_M^L(\underline{\Omega}) \quad (43)$$

where the generalized Clebsch-Gordan coefficient is given by

$$(L_A, M_A; L_B, M_B; L, M | J, N) = \sum_{\mu=-\lambda}^{+\lambda} (L_A, M_A; L_B, M_B | \lambda, \mu) (\lambda, \mu; L, M | J, N). \quad (44)$$

The set  $\{A_{\Lambda, N}^J | N = -J, \dots, +J\}$  transforms cogrediently to the set of spherical harmonics of order  $J$ . Using

$$(L_A M_A; L_B M_B; L M | 00) = \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} (-1)^{L_A - L_B + L} \quad (45)$$

we indeed find the expression (1 b) as a special case of (43), apart from a sign.

An irreducible interaction tensor  $\Theta^J$  of order  $J$  can be expanded as:

$$\Theta_N^J(\underline{\omega}_A, \underline{\omega}_B, \vec{R}) = (2J + 1)^{-1/2} \sum_{\Lambda} T_{\Lambda}^J(R) A_{\Lambda, N}^J(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega}), \quad (46)$$



where  $\Lambda$  is the set of quantum numbers defined in table 1. Because of the Wigner-Eckart theorem the expansion coefficients  $T_{\Lambda}^J(R)$  (reduced matrix elements) are independent of the magnetic quantum number  $N$ .

It is possible to apply the multipole expansion and perturbation theory in order to derive long range expressions for  $T_{\Lambda}^J(R)$ , thus relating this quantity to monomer properties. A simple example of such a procedure can be found in the appendix of ref.<sup>179)</sup>, where the induction contribution to the dipole moment ( $J = 1$ ) of an arbitrary Van der Waals dimer has been evaluated.

Because not much is known experimentally about general interaction tensors, and especially not about their long range behaviour, we will not pursue this line of approach, but rather give a brief review of the existing work which has concentrated on two different tensors: the pair dipole (order 1 tensor) and the pair polarizability (order 2 plus order 0 tensor).

## 5.2 Interaction Dipole Moments

The dipole moment of a Van der Waals dimer consists in principle of three contributions: the dipole moments of the two monomers and the interaction dipole moment. In the usual Van der Waals molecules the interaction dipole is in the order of  $0.1 \text{ D}$ <sup>159)</sup> which for a large part arises from induction. That is, permanent moments on the one monomer induce a dipole moment on the other. Obviously, this effect is absent in the case of a dimer consisting of two noble gases. Here the interaction dipole moment is an order of magnitude smaller and is largely due to the short range effects exchange and penetration<sup>180)</sup>.

The measurement of interaction dipoles by beam deflection<sup>181)</sup> gives an indication of the structure of the Van der Waals molecule. A recent example is given by Howard and coworkers<sup>182)</sup>, who experimentally established that the interaction dipole of  $(\text{CO}_2)_2$  is less than  $10^{-2} \text{ D}$ . Since it has sometimes been suggested<sup>159, 183)</sup> that the dimer is a T-shaped complex (a favourable configuration for quadrupole-quadrupole interaction, see above), they estimated the induction contribution to the dipole moment for this conformation (at  $R = 4.1 \text{ \AA}$ ) and found  $0.18 \text{ D}$  for this value. So they conclude that the dimer has most likely a staggered parallel configuration, which is in accordance with recent ab initio calculations<sup>184)</sup>.

Another experimental source for interaction dipoles is the measurement of pressure induced absorption<sup>185)</sup>. Strictly speaking this effect does not belong to the realm of Van der Waals complexes, because one measures here infrared radiation absorbed by *unbound* complexes. But since much can be learned about Van der Waals interactions from an interpretation of the data, we briefly review the work in this area.

First it should be noted that most of the experimental work on infrared absorption of gas mixtures has been restricted to cases where the constituent molecules themselves are not infrared active. Much work has for instance been done on mixtures of noble gases<sup>186)</sup> and noble gases with  $\text{H}_2$ <sup>187)</sup>. Noble gas mixtures show a broad band centered around  $100 \text{ cm}^{-1}$ . This is due to absorption by the translational motion of two unlike atoms relative to their joint center of mass. The same kind of translational band has also been measured in  $\text{H}_2$ -noble gas mixtures<sup>187, 188)</sup> and pure  $\text{H}_2$ <sup>188)</sup>.



Also rotational bands, with transitions lying in the region from 370 to 810  $\text{cm}^{-1}$ , have been observed<sup>188)</sup>. It is parenthetically interesting to note that the study of the translational band in  $(\text{H}_2)_2$  and  $\text{H}_2-\text{He}$  is of astrophysical interest, as the greenhouse effect on the outer planets is believed to be largely due to the translational band of these two dimers<sup>189)</sup>. (The temperature at the surface of these planets is about 150 °K  $\simeq 100 \text{ cm}^{-1}$ ). In the case of gases containing hydrogen one also observes the fundamental  $v = 0 \rightarrow 1$  band. This transition becomes (weakly) allowed under the influence of the interaction with the collision partner.

Much effort has been put into the explanation of the spectral line shapes<sup>190)</sup>, but it seems that the definite theory has yet to be established. In the meantime one can extract useful information from the first few moments of the spectral density, by applying the elegant theory developed by Van Kranendonk<sup>191)</sup> and Poll and Van Kranendonk<sup>192)</sup>. This theory relates the first moment to the derivative of the dimer dipole moment with respect to the intermolecular distance. The zeroth moment yields information about the square of the dipole moment. As this review is not the place to go extensively into the Van Kranendonk theory, we only note that, once the intermolecular potential surface and the interaction dipole field are known, — for instance by *ab initio* calculations — it is relatively easy to compute the moments of the spectral density. Since these are directly observable, the experiment of pressure induced absorption may serve as a check on the correctness of *ab initio* calculations, not only of the interaction energy, but also of the interaction dipole.

The first *ab initio* calculations on interaction dipoles were performed by Matcha and Nesbet<sup>193)</sup>. They considered the systems HeNe, HeAr and NeAr as “super-molecules” and did ordinary Hartree-Fock-LCAO-SCF calculations in the range  $R = 2.0$  to  $5.5a_0$ . Because of the Hartree-Fock approximation they did not obtain the dispersion contribution to the dipole moment (cf. sect. 2), but only exchange, penetration and overlap-induction contributions. Their *ab initio* dipoles could be fitted quite well by a single exponential, which supported the assumption made earlier by Van Kranendonk<sup>191)</sup>.

Later Byers Brown and Whisnant considered in detail the importance of dispersion, first theoretically<sup>194)</sup> by deriving Unsöld type expressions for the leading  $R^{-7}$  terms and subsequently numerically for HeH and HeHe. (In the case of HeHe the atomic contributions add up to zero, of course). At around the same time Lacey and Byers Brown<sup>195)</sup> considered also exchange and penetration contributions (in first order of perturbation theory) in addition to dispersion. They considered HeNe, HeAr, NeAr and ArKr in the range  $4.0$ – $9.0a_0$ . Since the collision induced absorption is largely due to complexes with intermolecular distances close to the scattering diameter  $\sigma$ <sup>196)</sup>, it is interesting to compare the values of the exchange dipole and the dispersion dipole at  $R = \sigma$ , (although the long range approximations which lead to the dispersion values are subject to serious doubt at such a short distance). Lacey and Byers Brown find that, except for HeNe the two contributions have opposite sign and that the dispersion dipole is about an order of magnitude smaller than that due to exchange.

Recent calculations by Berns et al.<sup>179)</sup> show that also for the He– $\text{H}_2$  system the dispersion contribution is small. At long range it is completely dominated by induction, at short range by overlap effects. The calculations of Berns et al. have been performed by the VB approach mentioned above<sup>63)</sup>. No perturbation theory or multipole expan-



sion was applied, although the VB method makes it possible to interpret the results in the usual long range terms plus exchange and penetration. In this manner it was found that the VB contribution which corresponds in the long range to the  $R^{-7}$  dispersion term completely failed to have an  $R^{-7}$  dependence from 3.7 Å ( $7a_0$ ) inward. This was surprising as the corresponding VB induction term kept its  $R^{-4}$  behaviour, predicted by long range theory, to much shorter distances. In any case, these VB calculations have shown that a very good description of the interaction induced dipole of the  $\text{HeH}_2$  complex requires only the inclusion of first order exchange, charge cloud penetration and — as the only second order term — induction. Since all these terms are accounted for in the supermolecule SCF approach such an approach seems to be ideally suited for routinely obtaining accurate dipole moments. However, when such calculations were undertaken in our institute<sup>196)</sup> a (somewhat unexpected) difficulty arose. Interaction dipole moments appeared to be much more sensitive to the basis set superposition error than interaction energies, and hence large and well balanced basis sets had to be employed. It may well be that inadequate basis sets form the source for the unreliability of the Matcha-Nesbet results<sup>193)</sup> at larger  $R$ -values.

However, once one is aware of the problem the basis set superposition error can easily be checked by a ghost molecule treatment<sup>63, 108–110)</sup>. Proceeding in this manner it was found<sup>196)</sup> that the spectral moments computed from the SCF results for  $\text{HeH}_2$  led to good agreement with the available experimental data. The outcome of the ab initio calculations also suggested parameters in the analytic representation of the dipole moment, which in a few respects differed considerably from those used so far in the interpretation of the experiments. When these new parameters will indeed prove to describe the experiment better than the existing ones, it will be yet another example of how the interplay of ab initio calculations and experimental work can be useful.

### 5.3. Pair polarizabilities

The influence of Van der Waals interactions on the polarizability of interacting molecules manifests itself in deviations from the Clausius-Mosotti equation<sup>197)</sup>, in the Kerr effect<sup>198)</sup> and in collision induced light scattering<sup>199)</sup>. Although measurements of these effects are all performed on bulk systems in thermodynamical equilibrium and not on Van der Waals molecules per se, we will nevertheless say a few words about pair polarizabilities, because, just as in the case of the collision induced IR absorption, much can be learned about Van der Waals interactions from the comparison of experimental and computational results.

In a pioneering paper<sup>200)</sup> Jansen and Mazur established the quantum mechanical basis for the effect of molecular interactions on the polarizability of spherical atoms. Using long range theory (no intermolecular exchange, Rayleigh-Schrödinger perturbation theory and only the first term in a multipole expansion of the intermolecular interaction) they derived an expansion of the pair polarizability as a power series in  $R^{-1}$ . The first two terms (in  $R^0$  and  $R^{-3}$ ) are the same as those obtained from classical electrostatics, the quantum mechanical effect of dispersion appears in the third ( $R^{-6}$ ) and higher terms. In a subsequent paper<sup>197)</sup> Mazur and Jansen applied their result to



the dielectric constant appearing in the Clausius-Mosotti equation, making a virial (density) expansion of this constant. They showed that the dielectric constant depends on the trace of the pair polarizability tensor, or rather, on the change in this trace caused by varying  $R$ . So, the dielectric constant provides information about the isotropic ( $J = 0$ ) part of the polarizability tensor. (It is interesting to note that the depolarized Raman intensity depends on the anisotropic ( $J = 2$ ) part of the polarizability tensor, and hence it is also experimentally convenient to separate the polarizability tensor into irreducible components.) When later dielectric second virial coefficients  $B_\epsilon$  were measured<sup>201, 202)</sup> for He, Ne, Ar, Kr, H<sub>2</sub> and N<sub>2</sub>, it was found that the results predicted by long range theory were considerably at variance with the experimental findings. It was therefore suggested<sup>201)</sup> that short range effects could not at all be neglected. And indeed, a finite field Hartree-Fock supermolecule calculation on He<sub>2</sub>, (including exchange and penetration)<sup>203)</sup> yields  $B_\epsilon = -0.093 \text{ cm}^6 \text{ mol}^{-2}$  at room temperature, compared to the experimental result  $B_\epsilon = -0.06 \pm 0.04$ . (The long range result has a positive sign, indicating that long range theory predicts the isotropic polarizability  $\alpha$  to increase with decreasing distance  $R$ , whereas  $\alpha$  decreases<sup>203)</sup> in the range of physical interest.)

Other ab initio calculations on the Hartree-Fock level of  $B_\epsilon$  for He<sub>2</sub><sup>204–206)</sup> also gave good agreement with the experimental results at room temperature, but at 4 °K a serious disagreement between theory and experiment appeared, which cannot be explained by approximations in the calculations. It has been suggested that the experimental data at 4 °K have to be reinterpreted<sup>204)</sup>. Recent ab initio calculations including correlation<sup>207)</sup> give  $B_\epsilon = -0.06 \text{ cm}^6 \text{ mol}^{-2}$  at 322 °K; so this value is now firmly established, experimentally as well as theoretically.

Whereas the dielectric constant probes essentially the  $R$ -dependence of the *isotropic* polarizability, the collision induced depolarized Raman scattering depends on the increment in the *anisotropy* of the polarizability with varying  $R$ . Depolarized Raman scattering of noble gases has first been observed by MacTague and Birnbaum<sup>208)</sup> in 1968, and later investigated for many gases<sup>209)</sup>. Very recently also polarized Raman intensities have been measured for Ne<sub>2</sub><sup>210, 211)</sup> and He<sub>2</sub><sup>212, 213)</sup>.

It is remarkable that short range forces, such as exchange and penetration, seem to have much less influence on the anisotropic than on the isotropic part of the polarizability. This has been observed in the interpretation of Raman data<sup>213)</sup> as well as in the results of ab initio calculations including correlation<sup>207)</sup>.

Several calculations of the polarizability tensor of noble gas dimers have been made<sup>214–216)</sup> which do include charge penetration, but not exchange. The work by Oxtoby and Gelbart<sup>214)</sup> is based on the concept of polarizability density. However, as pointed out by Sipe and Van Kranendonk<sup>217)</sup>, this concept, borrowed from macroscopic dielectric theory may lead to erroneous results for moments of order higher than 1. Similar criticism has been raised by Buckingham and coworkers<sup>216)</sup>, who have introduced instead a model based on perturbed (by the external field) atomic charge densities. They have calculated the collision induced polarizabilities of He<sub>2</sub> and Ar<sub>2</sub>, without exchange, and have found an anisotropy which is in excellent agreement with recent experimental data for He<sub>2</sub><sup>213)</sup> exhibiting again that exchange does not affect the anisotropy much at distances of physical interest.

Finally, it must be pointed out that theory and experiment are not yet in complete agreement with regard to the trace of the pair polarizability of He<sub>2</sub>. The most



complete quantum chemical treatment to date<sup>207)</sup>, one including correlation, is not fully consistent with recent polarized Raman data<sup>213)</sup>, which is surprising, since less complete (Hartree-Fock level) quantum chemical treatments<sup>203, 204, 218)</sup> account very well for the observed data<sup>213)</sup>. This is the more surprising as the correlation calculations give complete agreement with the experimentally determined second dielectric virial coefficient  $B_\epsilon$ , whereas the calculations on the Hartree-Fock level are here off by about 30 % (see above). An explanation for this discrepancy can perhaps be found in the fact that  $B_\epsilon$  depends linearly on the trace of the polarizability tensor, whereas the polarized Raman intensities are proportional to the square of this trace. Hence the two experiments constitute different tests on the trace. In the case of  $\text{Ne}_2$  there is still considerable disagreement between experiment<sup>211)</sup> and ab initio calculations<sup>218)</sup>, for the isotropic as well as for the anisotropic parts of the polarizability.

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## 6 Appendix

*Proof of the invariance of the function  $A_A(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega})$*

Consider a molecule with orientation  $\underline{\omega}_1 \equiv \{\alpha_1, \beta_1, \gamma_1\}$ . When we rotate this molecule over the Euler angles  $\underline{\omega}$ , the set of Euler angles  $\underline{\omega}_2$  describing the new orientation of the molecule, may be obtained from the matrix equation:

$$\underline{R}(\underline{\omega}_2) = \underline{R}(\underline{\omega}) \underline{R}(\underline{\omega}_1), \quad (\text{A1})$$

where  $\underline{R}(\underline{\omega}) \in \text{SO}(3)$  stands for a  $3 \times 3$  rotation matrix.

The Wigner D-matrices, defined in equation (2), belong to the Hilbert space  $L^2[\text{SO}(3)]$ . With a rotation  $\underline{\omega}$  of the molecule one can associate an operator  $\hat{R}(\underline{\omega})$  on this Hilbert space by defining:

$$\hat{R}(\underline{\omega}) \underline{D}^L(\underline{\omega}_2) \equiv \underline{D}^L(\underline{\omega}_1) \quad (\text{A2})$$

(This is Wigner's convention.) Realizing that  $\underline{D}^L(\underline{\omega})$  is a short-hand notation for  $\underline{D}^L(\underline{R}(\underline{\omega}))$ , and recalling that  $\underline{D}$  is a representation of  $\text{SO}(3)$ , we find, invoking (A1),

$$\hat{R}(\underline{\omega}) \underline{D}^L(\underline{\omega}_2) = \underline{D}^L(\underline{\omega})^{-1} \underline{D}^L(\underline{\omega}_2) \quad (\text{A3})$$

or:

$$\hat{R}(\underline{\omega}) D_{M,K}^L(\underline{\omega}_2) = \sum_{M'} D_{M',M}^L(\underline{\omega})^* D_{M',K}^L(\underline{\omega}_2). \quad (\text{A4})$$



From (A4) we draw the important conclusion that every column of a D-matrix is an irreducible tensorial set of order  $L$ , transforming contragrediently to the set of spherical harmonics of the same order. Indeed, if we take  $K = 0$ , and use that<sup>17)</sup>:

$$D_{M,0}^L(\alpha, \beta, \gamma) = C_M^L(\beta\alpha)^* , \quad (\text{A5})$$

we find the complex conjugate of the usual transformation equation for spherical harmonics.

The Wigner 3j-symbol is often defined as the coefficient coupling a product of three irreducible tensors (of the same variance) to an invariant<sup>46)</sup>. Invoking this definition, it immediately follows that the function  $A_\Lambda(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega})$  is an invariant.

However, a more explicit proof is obtained by rotating the D-matrices and the spherical harmonics appearing in the definition (1 b) of  $A_\Lambda(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega})$  by using Eq. A4, and subsequent application of the following relation<sup>17)</sup>:

$$\begin{pmatrix} L_A & L_B & L \\ M'_A & M'_B & M' \end{pmatrix} = \sum_{M_A, M_B, M} D_{M'_A, M_A}^{L_A}(\underline{\omega}) D_{M'_B, M_B}^{L_B}(\underline{\omega}) D_{M', M}^L(\underline{\omega}) \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \quad (\text{A6})$$

This shows that rotation of the dimer over  $\underline{\omega}$  leaves the function  $A_\Lambda(\underline{\omega}_A, \underline{\omega}_B, \underline{\Omega})$  invariant.

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